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NOTICES.

The Institution as a body is not responsible for the statements of opinion expressed in any of its publications.

Copyright.—Publication of abstracts of Papers and articles appearing in the Journal is permitted, provided that acknowledgment is made to the Institution of Petroleum Technologists.

Papers and Articles.—The Council invites Papers and Articles both for reading at Ordinary Meetings of the Institution and for publication in the Journal. All Papers, whether for reading or publication, will be submitted to a referee appointed by the Publication Committee.

The Institution has published a brochure "Instructions for the Guidance of Authors" containing details of recommended practice in the preparation of Papers for publication. Copies of this brochure will be supplied on request.

Pre-Prints.—Advance proofs of Papers to be read at Ordinary Meetings are generally available about a week before the Meeting. Members wishing to be supplied with these pre-prints are requested to notify the Secretary.

Abstracts.—Members and Journal Subscribers desirous of receiving the Abstracts printed on one side of the paper only, can be supplied with these at a charge of 10*s.* per annum per copy, payable in advance.

Issue of Journal.—Members whose subscription is not in arrear receive the Journal free of cost. A member whose subscription is not paid by March 31st of the year for which it is due is considered to be in arrear.

Changes of Address.—Members are requested to notify any change of address to the Secretary.

Benevolent Fund.—The Benevolent Fund is intended to aid necessitous persons who are or have been members of the Institution, and their dependent relatives.

The Fund is raised by voluntary annual subscriptions, donations, and bequests, and all contributions should be sent to the Secretary of the Institution at Aldine House, Bedford Street, London, W.C. 2. The Fund is administered by the Council through the Benevolent Fund Committee, and all applications in connection therewith must be made on a special form which can be obtained from the Secretary of the Institution.

Appointments Register.—A register of members requiring appointments is kept at the offices of the Institution, and every effort is made to assist members of the Institution in search of employment.

Members who desire their names and qualifications to be included in this register are requested to apply to the Secretary for the Form of Application for Registration, if they have not already done so. Members residing in the London area are asked, if possible, to return this Form in person and make themselves known, together with their requirements, to the Secretary. It is also requested that members should notify the Secretary immediately they have obtained an appointment.

In submitting names of candidates to prospective employers it is understood that the Institution accepts no responsibility and gives no guarantee.

Library.—The Institution's Library may be consulted between the hours of 9.30 a.m. and 5 p.m. daily. (Saturdays, 9.30 a.m. to 12 noon.)

APPLICATION FORMS FOR ADMISSION.

The Council desire to direct the attention of members who Propose or Second an Application Form for admission to the Institution to the importance of sending a covering letter for the guidance of the Election Committee.

STUDENTS' PRIZES.

Students are reminded that Papers submitted for the Students' Medal and Prize, and for the Students' Prize presented by Mr. T. C. J. Burgess, must be received at the Institution not later than 30*th September*, 1935. Two copies must be forwarded of each Paper submitted.

Full particulars of the Conditions of Award were printed in the February, 1935, *Journal*, or may be obtained from the Secretary of the Institution.

Mr. C. T. BERRY is home from Iraq.

Mr. F. G. CLAPP, who has been conducting geological studies in the West Indies, has returned to the United States.

Dr. G. Frischnecht has left Trinidad and is now in Switzerland.

Mr. J. J. L. HAMILTON has returned from Japan.

Mr. A. E. HEWITT has left Japan and is now in Singapore.

Mr. NIELS MATHESON has returned to Venezuela.

Mr. H. H. MOOR has left Canada for France.

Mr. J. G. WALTON has returned to Ecuador.

Mr. J. B. WILLIAMS has left for Burma.

Mr. H. WOODFIELD is home on leave from Japan.

The Secretary would be glad to learn of the addresses of the following members: J. M. Brown, M. Jawad Jafar, J. C. Jones, P. B. M. Linton, A. MacLean, W. J. Reynolds, K. A. Spearing, and A. C. Vivian.

ASSOCIATED STUDENTS.

In order to enable junior employees of petroleum companies to participate in the activities of the Students' Section of the Institution, the Council has approved "Associated Students" of this Section.

Associated Students will be entitled to receive notices of and to attend meetings of the Students' Section, and to make use of the Institution Library. They will not receive the *Journal*, and will not be eligible for Students' Prizes.

The annual subscription of an Associated Student is 7*s.* 6*d.*, payable on October 1st, and should be sent to the Honorary Secretary, Students' Section (London Branch), Mr. B. C. Ferguson, St. Helens Court, Great St. Helens, London, E.C. 3.

There is at present no age limit for Associated Students, but they will be required to proceed to Student Membership or Associate Membership (according to age) before the expiry of two years from the date of their becoming Associated Students.

ARTHUR W. EASTLAKE.
Honorary Secretary.

CONGRÈS INTERNATIONAL DES MINES, DE LA MÉTALLURGIE & DE LA GÉOLOGIE APPLIQUÉE.

The Seventh International Congress of Mining, Metallurgy and Applied Geology will be held in Paris from 20th to 26th October, 1935. M. HENRY LE CHATELIER is President of the Congress, and the President of France, M. LEBRUN, and Members of the Government have accorded their patronage.

The Congress comprises three Sections, which include the following Subsections having particular reference to petroleum :

MINING SECTION : Sect. IV. Petroleum :—Drilling; Production; Recovery Methods; Transport and Storage.

APPLIED GEOLOGY SECTION : Petroleum Geology; Geophysics.

The programme of the Congress includes Works visits and post-Congress tours to various centres. The subscription for individual members is 150 francs for membership of one Section and 50 francs for each additional Section. Full particulars may be obtained from the Secretary, Congrès International des Mines, etc., 13 rue de Bourgoyne, Paris (VII^{e}).

"STANDARD METHODS FOR TESTING PETROLEUM AND ITS PRODUCTS."

The third edition of the Institution's handbook on the methods for testing petroleum and its products has just been published. Since the publication of the second edition in 1929 the Chemical Standardization Committee has been actively engaged in consideration of the existing methods and in the investigation of new methods for specific tests. The results of this work are incorporated in the new edition, which contains nearly 100 pages more than the previous book. Among the new tests are those for Greases (Ash, Consistency, Drop Point, Free Alkali and Acid), Knock-Rating, Existent and Potential Gum in Motor Fuels, Cold Test of Motor Fuels, Dilution of Crankcase Oil, Vapour Pressure, Tests for Liquid Asphaltic Bitumen, and Viscosity in Kinematic Units.

The opportunity has been taken to rearrange the various tests in alphabetical order in preference to classification under products, in order to avoid the large amount of cross referencing under the old system.

A new section has been included for "Tentative" methods, and contains details of tests which are required but regarding which further experience is necessary before they can be considered as " Standard."

Copies of the book, which is bound in cloth, can be obtained from the offices of the Institution, price 7*s*. 6*d*. (To Members of the Institution, 5*s*. 0*d*.) Postage 6*d*. extra.

DEUTSCHE GESELLSCHAFT FÜR MINERALÖFORSCHUNG.

The Deutsche Gesellschaft für Mineralöforschung extends an invitation to the Members of the Institution of Petroleum Technologists to attend its General Meeting in Berlin on the 26th to 28th September, 1935.

The subjects for discussion will include :—

Geology and Geophysics; Prospecting and Drilling; Bituminous Materials; Transport Storage and Distribution; Diesel Fuels; Testing and Nomenclature.

Full particulars of the programme may be obtained from: Professor Dr. Ubbelohde, Deutsche Gesellschaft für Mineralöforschung, Dorotheenstrasse, 40 Berlin.

STORAGE AND USE OF LIQUID FUEL.

In 1920 the Fire Offices' Committee issued their "Recommendations respecting the Storage and Use of Liquid Fuel." Since that time considerable alterations have taken place in the use of liquid fuel in boiler furnaces in relation to its storage and in the installation of the plant. In view of these changes the Committee considered it advisable to revise their recommendations, and have now issued, in pamphlet form, "Definitions and Recommendations in Connection with Liquid Fuel for Furnaces using Oil having a Flash Point not below 150° F. (Closed Test)." The "Suggestions for the Safe Operation of Oil Burning Installations" contained in the pamphlet are also available on wall cards. Copies of the pamphlet and the card can be obtained on application to the Secretary, Fire Offices' Committee, 65 & 66, Watling Street, London, E.C. 4.

THE ASSOCIATION OF SCIENTIFIC WORKERS.

A joint Committee nominated by the Association of Scientific Workers, the Institute of British Executives, and the Engineers Study Group on Economics has undertaken an investigation into the problem of the unemployed scientific, technical and executive workers. The information at present available is fragmentary and members of the Institution who are unemployed are requested to send to Mr. Evans, Institute of British Executives, Swan House, 133, Oxford Street, London, W. 1, the following information : (*a*) Name and address, (*b*) Age, (*c*) Qualifications and field of work, (*d*) Period of unemployment.

CONTENTS OF OCTOBER JOURNAL.

The following papers are scheduled for inclusion in the October issue of the *Journal*:

"Viscosity and Stability of Drilling Fluid." C. W. WOOLGAR.

"Explosion of Mixtures of Combustible Gases with Air, by Nuclear Drops of Water and other Nuclei and by X-Rays." R. O. KING and GEORGE MOLE.

"A Wide Range Boiling Point Conversion Chart for Hydrocarbons and Petroleum Products." E. S. L. BEALE and P. DOCKSEY.

"Treatment of Water for Domestic Purposes in a Trinidad Oil-field." A. H. RICHARD.

"Cyclic Constituents of Petroleum Ceresin." JACOB MÜLLER and S. PILAT.

"Coking of Petroleum Residues." D. GLYNN JONES.

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ALBERTA OIL AND GAS DEVELOPMENT.*

By W. Calder, M.I.Min.E. (Member) † and R. M. S. Owen, B.Sc. (Associate Member).‡

As a gas and oil territory, Canada is one of the oldest producing countries in the world. The output of commercial gas and oil, however, declined considerably during recent years, and many competent authorities forecasted the eventual disappearance of the Dominion from the list of producing countries. Recent development, however, tends to show that such pessimistic views are a thing of the past, and it is reasonable to predict that Canada will again take a prominent position in the list of oil-producing countries.

The new Canadian area of production is at present confined to several small pools or fields in the vicinity of the Alberta Foothills of the Rocky Mountain uplift (Fig. 1). The principal development to date has been dry gas, for which there has been an ample local market both for domestic and commercial purposes. The most recent development, and one of the greatest importance, has been close to the City of Calgary, where, in an endeavour to locate the main body of high-grade oil proven during 1913–14, deep drilling revealed a very rich gas containing a large quantity of naphtha, a find at that time unique in the history of gas and oil development.

The presence of crude oil ranging from medium to heavy gravity has been proven at several widely separated points on the western plains, extending from the International boundary through Alberta to the far North, but at none of these has any considerable commercial production been developed to date. Finally, there are the extensive and well-known tar-sand deposits on the Athabaska River, which only await an economical method of extracting the oil *in situ* to obviate the necessity of excavation.

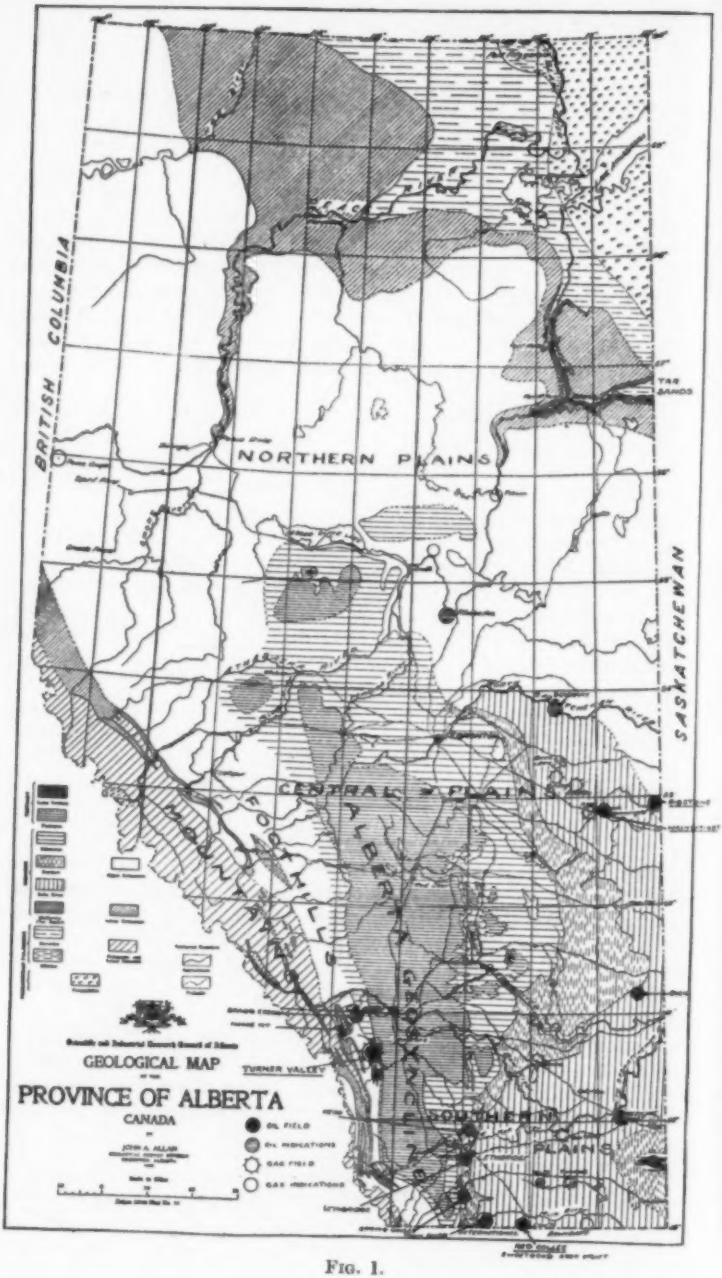
Production of Gas.

For many years the existence of gas seepages was known at different points along the foothills adjoining the Rockies, but no serious attempts were made to prove and develop the gas until an appreciable quantity was met during 1883 in a bore-hole drilled for coal at Langevin, now Alderson, Southern Alberta. Later on, in a well drilled for water at Medicine Hat, indications of gas were encountered, and encouraged the officials of the town to make representations to the Canadian Pacific Railway Company, who eventually co-operated in the drilling of the first test-well within the town limits. Commercial gas was encountered between 600 and 700 ft. from the surface. This confirmation of the presence of the gas led to the drilling of further wells, in all of which, when gas was discovered, the rock pressure was found

* Paper received March 15th, 1935.

† Director, Provincial Petroleum and Natural Gas Division, Alberta, Canada.

‡ Assistant Engineer, Provincial Petroleum and Natural Gas Division, Alberta, Canada.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SOUTHERN PLAINS
TAR SANDS
TURNER VALLEY
GEOLOGICAL MAP
PROVINCE OF ALBERTA
CANADA
OIL FIELD
OIL INDICATIONS
GAS FIELD
GAS INDICATIONS

FIG. 1.

to range between 250 and 275 lb. per square inch. The initial flow volume would appear to have been low, as no well exceeded an open flow of one million cubic feet per day.

Owing to the faulty drilling of these shallow wells, surface water after a time penetrated the gas horizon and the gas flow declined. Further and deeper drilling resulted in the discovery during 1905 of another gas horizon between 1000 and 1100 ft. from the surface. The initial rock pressure in the new horizon approximated 645 lb. per square inch, with a daily open flow of three to four million cubic feet per well. There are now twenty-six wells producing from the lower horizon within the town area, the rock pressure having declined to 369 lb. per square inch with an average open flow volume of one and one half million cubic feet per well per day.

During recent years water appeared in these deep wells in increasing quantity, particularly during peak load withdrawals when low temperatures prevailed. The intrusion of this water was generally considered to be due to water encroachment on a presumed underground structure. After a very careful review of all available data, Provincial Government Engineers found there was no conclusive evidence of an uplift in the formation and that the supposed encroachment of a water table in the gas horizon was untenable, the final conclusion being that the increasing danger was more probably due to the intrusion of surface water gaining access to the gas horizons through corroded casings. After considerable opposition, the repair suggestions of the Government Engineers were tried in one of the worst water-logged wells, and, the experiment proving successful, other wells were similarly repaired, with the result that the water danger has been eliminated and the useful producing life of wells in the central area considerably lengthened. The repairs consisted of lowering into the defective wells a smaller casing and filling the space outside the new casing to the surface with cement. The latter, being forced upward behind the casing under pressure, not only rose to the surface, but also passed outward into the formation above the gas horizon.

The foregoing repair work having disclosed the source of the intruding water, confidence in the gas potentialities of the area returned, and three new wells were drilled north-east of Medicine Hat. All of these were completed as gas producers at depths ranging from 1119 to 1250 ft., the daily volumes ranging from 2·9 to 3·7 million cubic feet per day, with an initial pressure of more than 500 lb. per square inch. These successful completions proved that the useful gas area around Medicine Hat was not limited, and tend to show a continuity in the gas sand outwards to distant points where fair productions of shallow gas have been obtained. With these proven indications, it is reasonable to anticipate that natural gas will be available for the requirements of the Medicine Hat district for many years, provided strict production methods are adhered to, while continuing the repairs of old defective wells and extending the productive area by the drilling of additional wells each year.

Considering how wasteful the Medicine Hat community has been in the past with this great gift of nature within the town limits—a frequent occurrence was the setting fire to the gas at the wells for the special benefit of prominent and other visitors—also at the present time never extinguishing the town street-lighting system, the rock pressure decline of the field

has been comparatively slight. No attempt having been formerly made to measure the gas when the area was first developed, it is impossible to give any data respecting the total quantity withdrawn from the field to date. During recent years, records show that the consumption ranges from 100 to 550 million cubic feet per month, or an average per month over the year of about 240 million cubic feet.

The development of the Medicine Hat field led to further prospecting, which resulted in commercial gas being discovered during 1908 at Bow Island at a depth ranging from 1850 to 1950 ft. These operations were under the guidance of Mr. Eugene Coste, who, when gas was proven, obtained a franchise from the City of Calgary for supplying that city with gas, thereafter organizing the Calgary Gas, Light, Heat and Power Company. The latter speedily drilled further wells, and towards the end of 1912 these had a daily open flow of 75 million cubic feet of gas at an original rock pressure of 745 lb. per square inch. With sufficient gas in sight, there was completed a 16-in. pipe-line to Calgary (168 miles), the gas being delivered by natural flow pressure not only to that city, but also to all towns along the route of the pipe-line.

The Bow Island area reached its peak during 1918, but from then it began to decline rapidly, and if the daily pull had continued, would eventually have resulted in the natural pressure being reduced to a point which would have necessitated the use of mechanical equipment to deliver the gas at Calgary. Fortunately, during 1922, when the Bow Island pressure had declined to 246 lb., the Foremost structure was discovered, and, on wells being drilled, open flow volumes of gas were developed ranging from 1½ to 10 million cubic feet per day at a rock pressure of 660 lb. per square inch. The discovery of this gas pool immediately reduced the daily pull on the Bow Island field. Now, on account of excess gas in the Turner Valley field being available, gas withdrawals from both these areas have been discontinued, and the gas is held as a reserve for the future. The Foremost discovery was timely, as the reserves of gas in the Bow Island field are estimated to have been depleted to 6000 million cubic feet, while the production of the area must have approximated 36,000 million cubic feet.

Immediately the excess Turner Valley gas became available for Calgary, or any other market, the Gas Company commenced a thorough overhaul of the Bow Island field, many of the old defective wells were abandoned by plugging off with cement, the remaining wells being tubed and cemented to exclude the water from the surface and shallow horizons from entering the wells and passing down to the gas sands. On completion of the well repairs in 1930, the Company started the repressuring of the area with excess gas from the Turner Valley. To date of writing, a total of 7259 million cubic feet has been forced into the depleted sands and the area pressure increased from 246 to 478 lb. per square inch.

In mid-northern Alberta, although gas in quantity is known to exist at several points, the only district being drawn on at present is that of Viking. Here commercial gas was first developed during 1914 at a depth of 2100 ft., with a rock pressure of 733 lb. per square inch and daily volumes per well ranging from one to eleven million cubic feet. The gas is piped to Edmonton and intervening towns through a line about 77 miles long. The average daily demand throughout the year approximates 16½ million

cubic feet, and as the supply is not supplemented from other areas it has been evident for some time that with an increase in the demand the economic producing life of the field would be shortened. This hazard, however, need no longer be feared, as other areas where gas in quantity has been proven will soon be coupled up to the distributing system, thus materially reducing the pull on the Viking area, and thereby considerably extending its producing life without fear of accelerating water encroachment by over-pulling of the wells. One of the areas referred to has been developed at Kinsella, 12 miles east of Viking, where the first completed well shows an available volume of 21 million cubic feet per day with a closed-in pressure of 780 lb. per square inch. Another very promising area which remains to be opened up lies to the north-west and north of the present Viking field.

In Alberta, the other known and partly developed gas areas are Redcliff, Cypress Hills, Brooks, Wetaskiwin, Fabyan, Wainwright and Ribstone. Indications have also been met at many other points in the south and central parts of the province. Finally, there are good evidences of gas in commercial quantities being present in the vast area extending north from Edmonton to Peace River and McMurray—an area in which no deep drilling has been done to date. The gas indications so far encountered have been met in shallow wells, and as these are very widespread, all tend to justify the forecast that, with an increase in deep prospecting, other rich gas areas will be discovered to further augment the supplies now in sight and assure for many decades not only reserves for the increasing domestic and industrial demands in Alberta, but also for export to other provinces.

Production of Oil.

Although an immediate market in most inhabited areas can usually be found for natural gas, and it can be classed as a product of high commercial value, the search for gas has never had the same attraction for prospectors as has been given to the finding of oil. For some time prior to 1900 endeavours to discover oil were diligently prosecuted all over Western Canada, but the time and money spent in most of these efforts were without any commercial results. In a measure this lack of success would appear attributable to inexperienced directive personnel, faulty technique in well drilling and the blind location of wells without any preliminary survey of the territory. In many cases the cause for this misdirection of energy and money was apparently due to stock manipulators who had no sincere wish to develop oil production. Most of the above prospecting, although of no commercial value, resulted in the proving at depth of oil indications at widely separated points, thus indicating the probability of paying production being discovered when wells are carefully located and drilled under the supervision of experienced personnel who will take all precautions to isolate water by cementation—also to overcome the varied conditions which always accompany pioneer deep well-drilling.

To date only three oil-producing areas have been developed. These are Turner Valley, Red Coulee and Wainwright. The presence of oil-bearing formation has also been confirmed at Ribstone, Oyen, Duvernay, Skiff and several other points in the south-west of the Province.

Operations at none of these, however, have been persisted in, despite the fact that the indications were in all cases very promising and, if further tests had been drilled around these discoveries, there is every probability that remunerative pools would have been opened up.

Turner Valley.

The Turner Valley area was discovered during 1913, when a light crude oil of 0·770 specific gravity was encountered at about 2400 ft. This was the cause of the wild stock gambling boom of 1914. The collapse of the latter and the advent of the Great War stopped operations, and it was only during 1922–23 that a renewed attempt was made to further prove and extend the 1913 find.

The development of the known light crude horizon, however, apparently did not appeal to those undertaking the prospecting in the Royalite well No. 4. This neglect may be due to the daily production from these horizons showing less than 100 barrels per well per day and deeper drilling was continued—presumably with the hope that more productive horizons would be encountered at depth. At that date the general opinion in other parts of the world was that if crude oil production was not encountered within the first 200–300 ft. in a limestone body it would be useless to drill deeper. This opinion being general would also appear to have been accepted as applicable to the Turner Valley. However, contrary to expectations, at 321 ft. in the lime (3740 ft. from the surface) there occurred a sudden outburst of wet gas under high pressure. Attempts were made to get the well under control, but these were delayed —first through lack of appliances, and secondly owing to the gas catching fire and consuming all the drilling equipment and derrick. Under considerable danger, the fire was eventually extinguished and the well brought under control on the 30th November, 1924. It is necessary to here note that besides the damaged 8¼, 6¼ and other casings, there was left in the well the drilling tools and 5000 ft. of steel drilling cable which dropped to the bottom when the fire occurred. All of this equipment must have considerably obstructed a free flow from the well, but on being controlled the latter gave a daily flow of gas amounting to 21½ million cubic feet. On this gas being passed through an improvised separator, 300 barrels of naphtha of 0·693 specific gravity were obtained daily, this quantity later on being increased to between 500 and 600 barrels daily when a properly designed separator was installed (Fig. 3).

Production from the Royalite No. 4 well continued to 1929, and records show that 911,313 barrels of naphtha were marketed during the productive period. So far no other well of its capacity and persistent production has been discovered in Alberta, and if the records of other world oil-producing areas are checked, it will be found that this well is not only unique as being the first to produce in quantity crude naphtha, but also must be classed as one of the big world producers.

As is usual with all new development, the sceptics were not long in circulating pessimistic views, all of which classed No. 4 as a freak well and forecasted that its productive life would be one of short duration; further, that no other wells of the same class would be developed in the

FIG. 2.

TURNER VALLEY, CENTRAL DISTRICT, MCLEOD 3 TO ROYALITE 23. LOOKING NORTH SHOWING SOUTH-WESTERLY STEEPLY DIPPING BELLY RIVER BEDS ON THE LEFT. SEPTEMBER, 1929.

[*To face p.* 758.

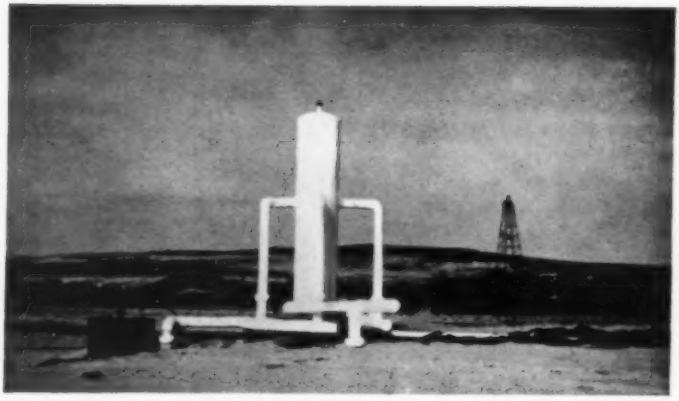

FIG. 3.
SEPARATOR AT ROYALITE NO. 4.

FIG. 4.
TURNER VALLEY, CENTRAL DISTRICT, LOOKING NORTH-WEST FROM SOUTH-EAST OF SHEEP RIVER. SEPTEMBER, 1929.

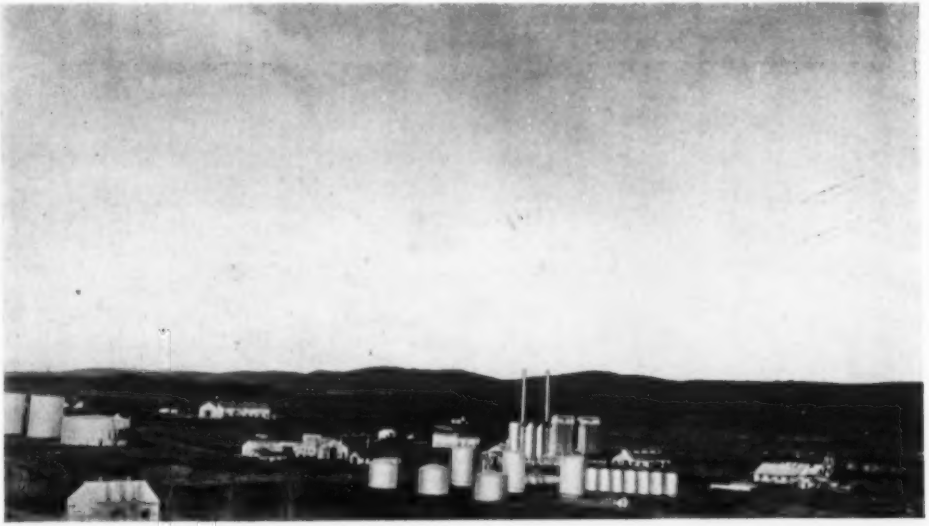

FIG. 5.

TURNER VALLEY SCRUBBING PLANT.

FIG. 6.
ABSORPTION PLANT, TURNER VALLEY.

Turner Valley. How far out these forecasts were will be appreciated when it is stated that to-day there are ninety producing wells located over an area approximately one mile wide and twelve miles long. A further wrong forecast was the view that no production would be obtained on the western flank of the structure. This fallacy has also been contradicted in the bringing in of several producers on the west side.

It is well to note that the foregoing ninety wells were not spaced at exact distances apart, and considerable indrilling has been done, particularly in two areas. In one of these thirteen wells were drilled on one quarter section—160 acres—where at the most four wells would have amply sufficed to drain the area. It can be safely stated that this unfortunate and extravagant development was solely brought about by the small area of leases—40 acres—such leases in many cases being further cut up unofficially into small blocks by land speculators.

Although No. 4 was got under control at the end of 1924, little or no interest was taken in the Turner Valley field until 1926. During that year several wells were started, but again interest dwindled, and it was only at the end of 1928 that the full significance of the steady increase in the Alberta oil production was appreciated. Prior to this, potentially good territory, not only in the Turner Valley, but also in other parts of the province, could have been obtained at reasonable royalty terms only. But with a return of public interest, valuations soared and all available acreage was blanketed by leases, and the genuine oil operator could only obtain from lease owners the drilling rights over land by agreeing to excessive royalties and making payments of bonus money for each acre leased.

The Turner Valley structure is a narrow overthrust fold running N.N.W. and S.S.E. with steeply dipping flanks, the east side ranging from 50° to 70° and undoubtedly overturned at depth, but on the west the dip is gentler. In the shallow wells the limestone formation was encountered around 3450 ft., while in wells located away from the crest greater depths had to be drilled.

Drilling Methods.—The majority of the wells were drilled with cable tools and took twelve to eighteen months to complete. The time occupied in drilling to production was unnecessarily long, this being mainly due to deflection arising from steep strata dips, and in many cases the inexperience and incompetence of the majority of the drillers and supervisors. Once the well deflected, the crooked part had to be tamped with boulders and cement and then redrilled. This operation had in most wells to be frequently repeated, and resulted in a great deal of valuable time being lost. The drilling time per well with cable tools has been reduced as the drillers have become more used to the formations.

During 1929 a great effort was made to displace cable drilling by rotary tools, but fortunately the majority of operators adhered to the former. Those who adopted the rotary must have found the cost excessive, and many must now be in a dilemma, as they have the unpleasant knowledge that the bottom of their rotary drilled wells are considerably off centre. Fortunately for the Turner Valley operator, water has at no time been a handicap in the work, the only water horizons encountered to date being those particular to surface formations. This water is easily excluded by cementing the surface column of casing, thus permitting the drilling to

proceed without any deep shut off with cement, other than that required for cementing in the producing column of casing at the top of the lime.

It is necessary to mention here that the Turner Valley area or other parts of the foothills present no unusual drilling difficulties, whether with cable or rotary tools, other than those usually met in steeply pitching formations and the wear on tools due to the hardness of the strata.

Well Pressures.—For a long time the impression was current that pressures in the Turner Valley were too high to be controlled, and that to close in any well completely would result in a bursting of the surface well fittings and casings. Such a calamity was certainly possible when operations were commenced, as the casing and well fittings then used were all of low test capacity and quite unsuited for pressures in excess of 500 lb. per square inch, but, as development progressed, all material used was of 3000 lb. test, and as at no time could the well pressure have exceeded 2500 lb. per square inch, there was no tenable excuse for the wells then not being completely closed in. This last assertion was made by the senior writer in 1928, after full and careful consideration of the few occurrences where drillers had reported that tools had been forced up from the bottom of wells by the gas, and also the fact that at the commencement of operations all the wells were drilled into production with no control-head at the well mouth. With the introduction of high-pressure equipment, there also came into service a new patent control-head. This well attachment, quite simple in construction, and designed on the principle of the oil saver used in the pumping of wells, permits of cable tools during the drilling being kept on the bottom of a well where there is present high formation pressure, also for the tools to be withdrawn without the risk of being suddenly forced upwards and jamming with the drilling cable. At the wells where this apparatus was used and pressure gauges were in position, at no time was any extraordinary pressure recorded.

Testing of Wells.—Formerly all operators vigorously opposed the complete closing-in of their wells for test purposes, the general practice being to operate at a pressure about one-fifth of 2500 lb. This opposition made it impossible to make any tests which would permit of the gas reserves being estimated, and it was only when the control of the natural resources was transferred to the province at the end of 1930 that the first complete closing-in of wells for test purposes was allowed by any operator. Even then, the first closed-in pressures were obtained only at wells in a small area. This test proved that the maximum pressure in the wells tested was not extraordinary, being only 1275 lb. per square inch. The testing of the wells in other areas was eventually accomplished in August 1931, when the highest pressure obtained on a twenty-four-hour shut-in was found to be 1885 lb. per square inch in a well not long completed and drilled in a newly developed part of the Valley remote from the first wells tested. More recent tests show that there has been a progressive pressure decline over all the field averaging about three-quarters to one and a quarter pounds per day.

In an endeavour to get the complete data necessary to estimate the reserves of gas, the Provincial Government was compelled to introduce temporary legislation without which the tests would never have been possible. The tests having been completed and the information collected

made available for all operators and investors who have participated in the development of the Turner Valley, the temporary legislation was rescinded. When initiating the tests the Government hoped that operators, once they had definite and unbiased data respecting the area as a whole, would appreciate the vital necessity of introducing efficient development of all wells under a unitization scheme, and thus assure for all participants an equal share in any benefits that might accrue in the event of a market being developed for the excess gas wasted. These worthy efforts were not appreciated by those who would have principally benefited, and considerable adverse publicity was circulated, misconstruing the efforts and insinuating that the endeavours of the Government were confiscatory. These distorted views, however, must now disappear, since the full data are available, confirming the necessity of efficient development, and also that a true knowledge of any gas-field demands accurate details of gas pressures and volumes of gas available in each well.

Where formerly the daily waste of gas exceeded 500,000 m. cu. ft., the quantity now destroyed has been reduced to approximately 250,000 m. cu. ft. per day, with an increased recovery of naphtha, as all operators now appreciate that it is only by maintaining high back pressure on the wells that the greatest recovery of naphtha is obtained. The daily waste of gas, although still considerable, shows a marked decrease, and fully justifies all the efforts that were made by the Provincial Government in their endeavours to obtain efficient production measures.

Many of the Turner Valley wells, particularly those of small diameter, suddenly stopped flowing, and quite as suddenly returned to the producing stage without any decrease in the wet gas flow. At first this peculiarity was presumed to be due to a freezing up at the well bottom, but when it was appreciated that such conditions could not occur without the presence of water, investigations were made which disclosed in all cases that bridges composed of ice and formation debris mixed with iron sulphide had formed. These bridges were invariably encountered at depths not exceeding 500 ft. from the surface, and their formation caused considerable thought, particularly on account of the ice, one theory advanced, which appears quite tenable, was that the ice originated from shut-off water leaking through at the casing joints in minute quantity, the cumulative drops being carried up by the gas and deposited as ice on the casing walls. That this theory is reasonable will be appreciated by all who have had experience in the handling of long columns of casing; the latter when withdrawn can invariably be unscrewed without difficulty—such slackening at the thread joints undoubtedly being due to the weight of the column.

Scrubbing of Gas.—As the wet gas issuing from the wells carries considerable sulphur, the percentage averaging 640 grains per 100 cubic feet of gas, it will be appreciated that the raw waste gas would be a very unpleasant and possibly dangerous product for domestic or other use. The gas, however, after leaving the naphtha separators is scrubbed in towers by being forced upward through a descending solution of bicarbonate of soda, which reduces the sulphur content to as low as five grains per 100 cubic feet (Fig. 5).

At present the available market for the scrubbed gas averages from 30 to 40 million cubic feet per day during mild weather and 50 to 70 million daily over the remainder of the year, when temperatures are low. As the

scrubbing units now working can handle only about 60 million cubic feet per day (any excess demand over the 60 million is filled by turning into the distribution system gas from the Bow Island field), all Turner Valley gas in excess of the 60 millions from which the naphtha has been stripped has to be destroyed. The latter is accomplished by conveying the stripped gas to a distance from wells and habitations where it is ignited. The sight of the burning flares, although now considerably reduced in size, is most awe-inspiring at any hour, but particularly at night-time, and a facile writer could obtain good inspiration for a treatise on waste.

Crude Oil.—One peculiar phase of development of the Turner Valley field is that the high-grade crude oil ranging in gravity from 35° to 50° Beaume, encountered at depths ranging from 2500 to 4500 ft., varying according to the position of the well on the structure, has been ignored by the operators. This lack of interest is possibly due to the oil being in very compact sandstones, which do not readily permit an immediate free flow of the oil. As the various oil horizons have been encountered and shut off in most of the deep wells, there is sufficient proof to justify the forecast that, when wells are drilled solely for crude oil production and the oil is recovered by efficient production methods, there will be established in this area the beginning of a remunerative oil industry which will outlast, in productivity, the present generation by many years. When it is considered that wells to develop the crude oil could have been quickly and cheaply drilled at costs ranging from $20,000.00 to $50,000.00 per well, it is a paradox that those responsible for development preferred to drill deeper wells at costs ranging from $175,000.00 to $200,000.00. As an example that the crude oil exists in abundance, one well has been in production since 1926, and up to the end of 1934 had produced more than 80,000 barrels. From the undermentioned figures it will be noted that the crude oil output from wells in this area has shown a slow but steady increase up to 1929, from which year the development has been affected by all efforts having been concentrated in the drilling of wells for wet gas production.

Turner Valley—Crude Oil Production.

1925	2926	barrels
1926	2609	,,
1927	38808	,,
1928	70734	,,
1929	72480	,,
1930	50545	,,
1931	26936	,,
1932	21694	,,
1933	23822	,,
1934	21896	,,

Lately there has been a renewal of interest in Turner Valley crude oil development, and in one well drilled specially for this production every endeavour was made to reduce the cost, with the result that the well was completed to 2880 ft. for a total outlay of $11,300.00. The well has now been in production eight months, and has produced over 4500 barrels nett, a quantity more than necessary to repay the cost of drilling after allowing for reasonable operating and other charges.

Naphtha Recovery.—One very significant and welcome change has developed from the field tests completed last year, in that the majority of operators, now realizing the wasteful production methods hitherto practised, are experimenting in an endeavour to reduce the extravagant and uncalled-for gas–oil ratio under which the naphtha has been produced.

The field tests also confirmed that a considerable quantity of naphtha was not recovered in the separators, this loss ranging from 0·05 to 0·25 gallon per m. cu. ft. of gas burnt, and as the loss must have been greater in the past, the quantity of naphtha ignorantly dissipated must have been very great. In an endeavour to eliminate the loss, the major operating Company has erected an absorption and rectifying plant capable of processing from 75 to 100 m.m. cu. ft. per day. Although very much deferred, the erection of this recovery plant indicates that sound endeavours are in progress to combat waste and introduce efficiency, and it is expected that these efforts will also extend to improvements in well production methods, and if these materialize, waste will be reduced to a minimum, thus reducing the incompetence and inefficiency which wastefulness entails (Fig. 6).

Economical Aspects.—Summing up the Turner Valley situation from a financial point of view, it is necessary to state that to date results are most unsatisfactory, as only a pittance has been repaid to investors by a few Companies. This lack of return is solely due to the over drilling of deep wells and to the deliberate neglect to explore the possibilities of the crude oil. Now that definite data is available on the wet gas development, all must appreciate the futility of such development and will concentrate in producing crude oil, a commodity for which there is a considerable market both in Alberta and the adjoining Prairie Provinces.

Prospective Areas.

Pekisko.—Although promising surface outcrops of formation parallel the Turner Valley for some distance west, no other productive area has been found in this direction. At Pekisko, approximately ten miles south of the Valley, a well drilled near the Prince of Wales Ranch encountered a very promising horizon at depth, the crude oil from which rose to near the surface. The production possibilities, however, are not known, as no continued test has yet been possible, presumed to be due to a serious deflection in the well. Similarly, to the north-west and close to Bragg Creek, crude oil in quantity has been discovered, but again engineering difficulties in the well prevented an efficient test. The area, Pekisko–Bragg Creek, has a range of approximately fifty miles, of which the Turner Valley—where the only intensive development has been done to date—represents twelve to fourteen miles. Outside of the latter only a few wells have been drilled, and with the exception of Pekisko and Bragg Creek none of these reached productive horizons. Most of the failures were undoubtedly due to inadequate equipment and inefficiency. When it is considered that the foothills extend for a distance of over 250 miles in Alberta, and that all along this length favourable geological conditions have been located, also in many places active gas seepages, it is not presuming to forecast that many other areas, possibly even more productive than the Turner Valley, will be developed in the future. The geology of the area, however, is very complicated, and before any deep tests are located an intensive and careful

survey over the particular area should be made by competent structural geologists. This necessity cannot be over-emphasized, as many of the prospect locations drilled on in the past give evidence that the selection of well sites must have been made without any previous intensive field investigation of these areas.

Another area, but of unknown potentialities, is that immediately to the east and bordering the foothills. It is expected that this strip may prove very narrow, but, inasmuch as the real source of the Turner Valley production has yet to be discovered, there is a possibility that wells drilled along this line of the foothills may develop production. With the foregoing vast area in the frontal ranges still unexplored at depth, the outlook for the production of crude oil is promising, and those undertaking the search will undoubtedly reap considerable profit.

Red Coulee.—To date the development at Red Coulee has resulted in only five producing wells. These, however, produced to the end of 1934 a total of over 200,000 barrels of oil, and prove that, although the daily production per well is low, commercial production can be relied on for a considerable period. Other wells drilled also encountered good inflows of oil, sufficient in quantity to produce from fifty to seventy barrels per day. These outputs, however, must have been considered unattractive, as the wells were abandoned after being drilled into bottom water at some depth below the oil horizon. The gravity of the Red Coulee oil is similar to that produced in the adjoining Kevin-Sunburst field, Montana, and averages 31° Beaume.

Due undoubtedly to the abandonment of the tests above cited, no extension of the Red Coulee productive area in Alberta has yet been made, but the discovery of a similar grade of crude oil in wells drilled at Lethbridge and Keho—sixty miles north-west, and also at Twin River—twenty-five miles west, indicate that there must be extensions of the Red Coulee area both north and west. The area, however, being outside the foothills belt, is similar to the prairie or plains country to the east—that is, the surface geology is masked with glacial drift, and outcrops of formation are lacking to guide the geologists in deciding where favourable structure exist underground. It would, therefore, appear that extensions to the Red Coulee area will be discovered only by means of chance drilling or by one or another of the scientific instruments which are being so extensively used in other countries for locating hidden structures. The chance location of wells, however, cannot be recommended, as such wildcatting will be found very expensive on account of the depth, 2000–3000 ft. of barren formation having to be drilled before productive horizons can be expected.

The crude oil discovered at other points in the province, Skiff, Oyen, Ribstone, Wainwright, Duvernay and Peace River, ranges in gravity from 14° to 25° Beaume. Although the indications at these different and widely separated points have been encouraging, the only areas where endeavours have been prosecuted to learn the production capacity of the sands are at Skiff, Ribstone and at Wainwright. At the first two the tests were not at any time of long enough duration to give the operators definite evidences respecting the oil flow capacity from the sands.

Wainwright.—At Wainwright, although production exists in eleven wells

spaced over a large area, operations have been erratic, and at none of the wells has an efficient pumping programme been attempted. As an instance, once a deep-well pump is placed in position, it is not considered necessary to withdraw the pump for repairs or the cleaning of the well bottom. During the short history of the field, one well was brought in which flowed 255 barrels of clean oil per day. This, however, was flooded out in less than a week owing to the breaking through of surface water which had never been efficiently cemented off. In all of the other wells the oil column rises 1200 ft., but at none has the daily inflow exceeded 35 barrels per day.

Although the rotary drilling system has been used in other parts of the province, Wainwright is the only area where it has been used almost exclusively. To date, only two wells have been drilled with cable tools. This apparent preference for water-flush drilling has no valid justification, as there is nothing in the underground formations at Wainwright, or any other part of Alberta, which would preclude the use of cable tools, provided the personnel are fully competent with this system of drilling and that the drilling, once started, is carried down expeditiously and water, when encountered, efficiently shut off. Undoubtedly the prejudice to percussive tools has been created owing to the original drilling in the field having been done with the rotary and to the rotary drillers, whose biased opinion was until recently the sole source of oil-field technical advice available to operators.

If the latter would only appreciate that the productive horizons are at about 2000 ft. from the surface, and that the oil over most of the field has a head of only 1200 ft., they would realize the danger of using a drilling system which introduces on the sand a hydrostatic pressure of nearly 1000 lb. per square inch. It is necessary to sympathize with the Wainwright operators, as they have had to pay exorbitant rates for the drilling of their wells, this high cost preventing the individual operator drilling further wells which would permit of production costs being reduced to an economic level, an impossibility under present conditions, as single wells have to carry the full burden of uncalled-for capital charges and excessive running overhead expense.

There is ample proof that the productive life of the wells will be of long duration, two having been in production for six years. If sufficient wells are drilled, at least six to each quarter section, or 160 acres, the returns, even at a low production of twenty barrels per well and the oil selling at the low price of seventy cents per barrel, are fully worthy of comparison with other investments.

The presence of crude oil formation having been demonstrated at Wainwright, Ribstone and Duvernay, there appears ample evidence in the opinion of the senior writer to justify the theory that there exists in this triangular area a vast underground seepage, the oil of which has insufficient pressure to pass upwards through the intervening strata and exude at the surface. Further, as the oil produced to date presents considerable volatility, this evidence permits the assumption of replenishment, possibly from a deeper source along lines of weakness in the underlying limestone formation.

Athabaska Landing.—Recently heavy crude was discovered at a depth of 1650 ft. near Athabaska Landing, and although the gravity of the oil

is low (12·1° Beaume), the discovery must be classed as one of importance as the sand, 50 ft. in thickness, should contain considerable oil. Gas in quantity, however, did not appear, and it is therefore very improbable that sensational daily productions per well will be obtained. The prospects, however, for small persistent wells, producing over many years, are encouraging subject to the sand being found continuous over a large area.

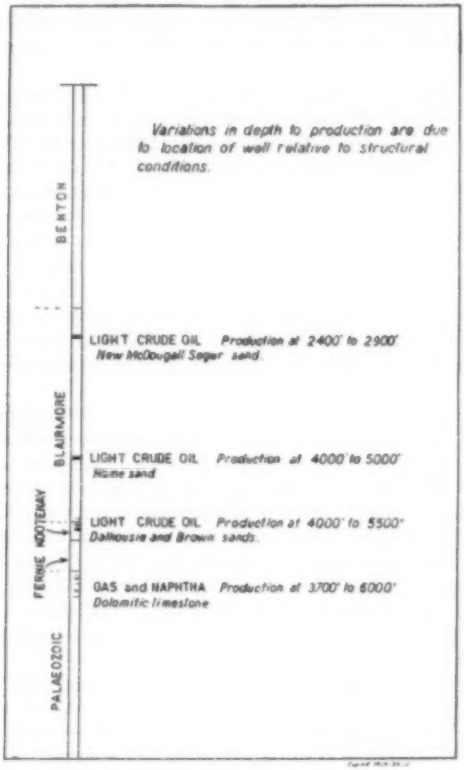
Variations in depth to production are due to location of well relative to structural conditions.
BENTON
LIGHT CRUDE OIL Production at 2400' to 2900'
New McDougall Segar sand.
BLAIRMORE
LIGHT CRUDE OIL Production at 4000' to 5000'
Name sand
KOOTENAY
LIGHT CRUDE OIL Production at 4000' to 5500'
Dalhousie and Brown sands.
FERNIE
GAS and NAPHTHA Production at 3700' to 6000'
Dolomitic limestone
PALAEOZOIC

FIG. 7.

GEOLOGICAL FORMATIONS IN TURNER VALLEY.

It is necessary to record that the presence of oil without water was made possible solely owing to the intervention of Government Engineers in demanding that the water be cemented off before the oil horizon was penetrated.

As regards prospects in the other heavy crude areas cited, further and more thorough testing will have to be done before it is possible to indicate the potentialities of the underground strata.

As an index of the progressive increase in crude oil production alone in Alberta, Fig. 8 gives the respective annual productions, and is sufficient

evidence that this industry is now on a permanent basis. As previously noted in connection with the Turner Valley crude oil production, a slight

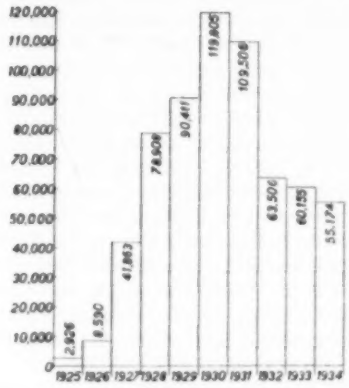

FIG. 8.

SUMMARY OF CRUDE OIL PRODUCTION ONLY, ALBERTA. BARRELS OF 35 IMP. GALS.

decline will be noted from 1931, the reason for this decline having already been referred to.

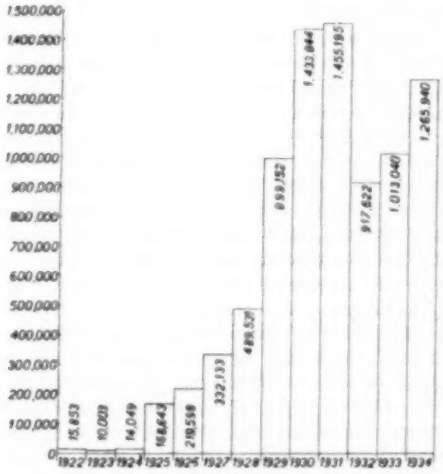

FIG. 9.

TOTAL ANNUAL OIL AND NAPHTHA PRODUCTION, ALBERTA. BARRELS OF 35 IMP. GALS.

Comparing the foregoing with the gross production of oil and naphtha given in Fig. 9, the great excess of naphtha will be noted, confirming the intensity of the development for this product alone.

Geology.

Physiographically Alberta may be divided into three regions as follows: (1) The mountains lying along the Alberta–British Columbia boundary; (2) the foothills, a narrow belt adjoining the former to the east; (3) the plains, occupying the remaining major part of Alberta.

The mountain region contains many peaks rising over 10,000 feet above sea level. The strata consists mainly of limestones and quartzites of Palæozoic age arranged as a series of blocks thrust over each other from the west. Very little drilling has been attempted in this region owing to the general early geological age and great thickness of the beds, the extremely broken-up nature of the structures, absence of suitable cover rocks and the general inaccessible nature of the country. Some drilling has taken place near Waterton Lake in the extreme south-west part of the province, where small production has been obtained from beneath an overthrust fault in beds of younger geological age than are exposed at the surface. It is, however, logical to state that large commercial production cannot be anticipated from the mountain region.

The foothills and plains regions have been the scene of considerable activity in the search for oil and gas. In recent years very complete records have been obtained of all drilling progress, including the collection and preservation of samples of the formations penetrated by all the wells drilled in the province. Chemical analyses of all waters, oil and gas encountered have also proved of practical value in correlation and in the solving of field problems.

The foothills form a narrow belt bordering the east side of the Rocky Mountains for practically their entire length, trending in a general N.W.-S.E. direction and averaging about 20 miles in width. The geological structure is complex, consisting of a series of longitudinal westerly-dipping, intensely compressed overthrust fault blocks which owe their origin to the pressure exerted by the mountain-building forces which uplifted the mountain region to their west. Some of these overthrusts exhibit great horizontal and vertical displacement, a case in point being Turner Valley, where beds as low as the Lower Carboniferous have been carried forward and now rest on Upper Cretaceous beds. Turner Valley is one of the most westerly of the foothill anticlines, and appears to be a drag fold developed along a low-angled thrust. The surface geological strata encountered in the foothills consists mainly of sandstones and shales of Mesozoic age.

Throughout the foothills the rocks are generally steeply dipping and highly consolidated, while the formations attain a greater stratigraphical thickness than they exhibit in the plains area to the east, owing to the fact that the former were deposited nearer the centre of the great geosyncline which once existed on the site where the Rocky Mountains now stand.

Although excellent indications have been found in many wells along the line of the foothills belt, the only commercial production obtained in this belt is at Turner Valley. Other promising structures remain to be tested, some with surface structure more pronounced and ideal for the accumulation of oil than can be seen in Turner Valley, and which may eventually prove equally productive.

The plains region embraces the large part of Alberta lying east of the

foothills, falling gently in a general east and north direction from a general elevation of about 4000 ft. above sea level at its western limit adjoining the foothills. Geologically the structure is much simpler than in the foothills, the strata being relatively undisturbed, the folding gentle and faults uncommon. Most of the plains area is covered by Mesozoic and Tertiary strata, and it is only in the north-eastern part of the province that Palæozoic and older rocks outcrop. The beds are less consolidated, and generally show a greatly decreased stratigraphical thickness compared with their representatives in the foothills.

In considering the structural features of the plains, the following may be mentioned. In Northern Alberta the formations gradually rise until Palæozoic, and finally the pre-Cambrian of the Canadian Shield are exposed in the extreme north-east of the province. Around McMurray on the Athabaska River occurs the well-known tar sands of Lower Cretaceous age resting upon Devonian limestone. Much of the drilling in this northern area have been attempts to reach this horizon down dip away from the outcrop, in the hope of finding a more liquid phase of the tar. Although good showings have been encountered in these wells, there has not been found so far structures of sufficient magnitude to concentrate the oil into commercial pools.

The discovery at Athabaska Landing, previously mentioned, appears to be the most promising development to date, and may be the forerunner of considerable prospecting which will prove whether the foregoing tar sand theory is tenable.

The eastern part of Central and Southern Alberta plains is dominated by the trough-like asymmetrical Alberta syncline; narrowest in the south and widening rapidly to the north, and representing the final filling up of the geosyncline previously mentioned, where deposits were laid down as late as Tertiary times. Most of the drilling in this area has taken place on the uprising eastern limb of this syncline and on subsidiary folds located on this main feature. A broad anticlinal fold is known to occur near the Saskatchewan boundary in the Ribstone area. In Southern Alberta a third structural influence is provided by the Sweetgrass Arch uplift, centring about the series of igneous plugs in the northern part of Montana, and extending as a nose over the International Boundary into Alberta, and giving rise to the oil-field at Red Coulee and folds containing gas further to the north.

As previously mentioned, the mantle of drift which covers the prairie country prevents the locating of underground structures unless deep test well-drilling is undertaken. A possible aid in overcoming this difficulty may be afforded by geophysical methods of prospecting. Initial work has already been done with magnetometer, seismic and torsion balance methods in different areas, but to date none of these has been tested by drilling, and until this has been done nothing definite can be stated respecting the future usefulness of these accessories as an aid to the geologist.

The possible existence of structures formed by deeply buried igneous intrusions similar to those exhibited around the Sweetgrass hills, and also the possible presence of pre-Mesozoic folding of the Palæozoic rocks, may be brought to light by geophysical means.

The vast area of Alberta (255,285 square miles) reveals beds of widespread

diversity in geological age. Varying conditions of deposition existed contemporaneously in different areas, so that the lithology of beds may vary greatly laterally; while some areas were land, other areas were receiving marine deposits. Local formational names are employed in different areas, and correlations from one area to another are still largely tentative, so that it is difficult to give a concise account of the geology to apply to the foothills and plains of Alberta within the confines of this paper.

Pre-Cambrian rocks, devoid of oil possibilities, outcrop in the north-east part of the province. The succeeding Palæozoic group of strata attain a great thickness in the western part of the province, the beds being mainly marine limestones and dolomites with some quartzites, while beds of anhydrite, rock-salt and shale are also found in the Devonian. Very few wells have penetrated beds below the top of the Devonian, and no well has penetrated the complete stratigraphical sequence to the pre-Cambrian except around the outcrop of the latter in the north-east. Our knowledge of the early Palæozoic rocks over the plains is very sketchy, although one well in Southern Alberta has penetrated to beds of Ordovician and probably Cambrian age after penetrating a lean oil shale in the Devonian, and a certain foothills well is testing beds believed to be low in the Palæozoic. The presence of oil in the Devonian at Fort Norman in the North-West Territories has led to the hope that the Devonian of Alberta may likewise prove productive.

A large break in the sedimentary record occurs at the top of the Palæozoic series when prolonged erosion ensued. Over large parts of Alberta beds of Carboniferous, Permian and Triassic age are missing, due either to original non-deposition or through the effects of the erosion mentioned above. Thus the succeeding Mesozoic strata are found to rest upon the Carboniferous in the foothills and the southern plains, while in Central and Northern Alberta Mesozoic strata are found overlying the Devonian. This unconformable contact between Palæozoic and Mesozoic strata appears to be associated with oil occurrences at Turner Valley, Twin River, Keho, Lethbridge, Skiff, Oyen and Wainwright. In Turner Valley the main gas and naphtha horizon is found at the top of the Carboniferous limestone beneath this unconformable contact in a zone of porous weathered dolomitized limestone overlain by chert, all suggestive of the erosion of an old land surface.

The succeeding Mesozoic Era was ushered in by the marine shale deposits of the Jurassic sea (Ellis or Fernie formations) which covered parts of Southern Alberta and the foothills. This was followed by the continental and shallow water deposits of the Lower Cretaceous (subdivided into Kootenay and Blairmore—in part—in the foothills), where deposits mainly consist of interbedded greenish-grey sandstones and shales with some workable seams of coal in the Kootenay of the foothills. To the north these deposits were in part replaced by marine beds, with corresponding changes in lithology. Sandstones of this age carry oil at Turner Valley and Red Coulee, where the Lower Cretaceous rest on Jurassic shales, and also at Wainwright and Ribstone, where these Lower Cretaceous beds rest directly on the Devonian. The bituminous tar sands of the Athabaska river form the basal member of beds of this age, again resting on Devonian. Gas and

shows of oil have been found at the same horizon at Pelican, Peace River and Smith.

Later deposits were the widespread marine shales of the lower part of the Upper Cretaceous (Benton or Alberta Shales) which covered nearly the whole of Alberta. Sands in the lower part have provided the gas in the Viking, Kinsella, Fabyan, Bow Island and Foremost fields, and have yielded oil at Keho with showings of oil elsewhere. Another sand near the top supplies the gas of the Medicine Hat field. Local vulcanicity occurred at the base of the Upper Cretaceous in the south-west part of the province.

Movements heralding the approach of the Rocky Mountain uplift caused shallowing of the above sea, and the upper part of the Upper Cretaceous (Belly River, Bearpaw and Edmonton formations) is composed mainly of great thicknesses of brackish and fresh-water sandstones and shales derived from the west, the beds becoming more marine to the east, the most westerly transgression of this eastern sea occurring during Bearpaw times. Thick and widespread coal seams occur in beds of non-marine facies. Beds of this age underlie most of the surface of Alberta.

Tertiary deposits of fresh-water soft shales and sandstones known as the Paskapoo formation are found in the centre of the Alberta syncline, and beds of similar and later age are found in the Cypress Hills erosional remnant. An unconformity has been found at the base of this formation in several places.

Pleistocene glacial deposits and unconsolidated clays, as previously stated, cover a great part of the province. The oil possibilities of the plains have been scarcely touched by the few wells so far drilled over this wide area.

Recent development in deep well-drilling should also make possible the drilling of certain structures where possible oil horizons were previously considered to occur too deep to warrant testing.

Prospecting Regulations.

The Prairie Provinces—formerly known as Prince Rupert's Land, and under the jurisdiction of the Hudson's Bay Company—were transferred to the Dominion Government on the advance westward of settlement. After the transfer, all land was sub-divided in quadrilateral townships containing thirty-six sections, each one mile square, or approximating this area, as the convergence of meridians demanded. Further, each section is again sub-divided into sixteen sub-divisions of forty acres in area.

On the sub-division of the land, there was reserved in perpetuity to the Hudson's Bay Company all of the surface and underlying minerals in Sections 8 and 26 of each township south of the North Saskatchewan River. A further relinquishment was made in favour of the Canadian Pacific Railway Company, who were also granted in perpetuity all the surface and mineral rights in every even numbered section in each township. Finally, lands patented by homestead settlers prior to 1887 also carried not only the surface rights, but also all minerals other than precious metals. After 1887 all mineral rights in homestead patents were reserved to the Crown.

The prospecting for gas and oil on Crown lands within the province is open to all on the filing of an application for a lease and the payment of fifty cents per acre for the first year's rental, the latter being $1.00 per acre for

the succeeding years. There is also a registration fee of $5.00 for each lease. Under the Regulations promulgated by the province in 1931, no lease can be less than 160 or more than 1940 acres. Prior to 1930 oil recovered from Crown land was not subject to any Crown royalty, commencing with the 1st of January, 1930, the royalty payable on nett production was at the rate of 5 per cent., and from the 1st of January, 1935, the rate has been raised to 10 per cent., and is now the same as that hitherto collected by the owners of alienated land. Natural gas produced from Crown lands is free from royalty payment, but with the rapid increase in the production of this useful fuel, it would be inconsistent if a royalty is not also charged on gas obtained from the public domain similar to that now paid to private owners on all gas recovered from alienated lands.

By the Provincial Regulations, drilling is not obligatory during the first fifteen months of any lease. Other easements subject to actual work being done are also provided for, the principal of these being the granting of credit against the lease rentals, such credit allowances being earned and based on the footage drilled in wells of over 1000 ft. in depth.

From surveys made to date, the prospects for metal mining in Alberta do not show that this industry will attain to any magnitude, and any mining revenue which the province will receive from the natural resources will depend on the efficient development of the different fuels already known to exist within the boundaries of Alberta. Indications are widespread, and show that these are available in considerable quantity, and their development, particularly that of oil and gas, should prove a valuable asset, and, furthermore, materially assist in solving the unemployment question in Alberta.

In a measure, it is regrettable that the transfer of the resources occurred at a time shortly after the world depression had commenced, resulting in a complete stoppage of all oil and gas development not only in productive areas, but also in prospecting. Alberta, however, is not unique in this set-back, and the latter, although regrettable, has one favourable feature, inasmuch as the delay has given the provincial authorities time to draft requisite regulations and organize the various departments controlling the development of the resources.

The regulations promulgated by the Provincial Government are based on those formerly in force under Dominion supervision, and any additions are such as were found necessary to bring these up to date for efficient development, so as to avoid in the future a repetition of the past unsatisfactory operating methods. Assurance is, therefore, given to all bona-fide operators that in undertaking development of the resources of Alberta they can rely on sympathetic Government consideration in all their operations.

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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

TRINIDAD BRANCH.

THE Forty-first General Meeting of the Trinidad Branch of the Institution of Petroleum Technologists was held at the Apex Club, Fyzabad, on Wednesday, January 30th, 1935, Commander H. V. Lavington, Branch Chairman, in the Chair.

The following paper was read.

THE RELATIONSHIP OF MUD TO ELECTRICAL CORING.

By H. C. H. THOMAS, M.A., A.R.S.M. (Associate Member).

The subjects which it is proposed to discuss in this paper are frequently discussed individually in one form or another, but, it seems to the writer, seldom in combination.

Mechanically, physically and chemically, mud is the primary agent in modifying the electrical characteristics of the formations, when they are exposed by the drill, and for this reason any expression of opinion on an electrical well survey, to be of value, must involve a knowledge of mud conditions.

It is proposed to outline the effects of mud on electrical profiles, and although it may be superfluous, it is desired to direct attention to the use of the word " specific " when describing resistivity and porosity.

Electrical logging sets out to determine, not the actual resistivity (*i.e.* resistance offered by a unit volume of the material comprising the rock) or the actual porosity of a rock (*i.e.* percentage pore-space by volume in a relatively uncompacted material), but specific values of these properties, that is to say that they are " of limited force and application," and they could be precisely evaluated only if all outside influences could be reduced to mathematical expression.

This is as impossible as it is for a geologist to deduce from core samples a precise forecast of production.

One other point might be made. The word porosity is often used in a loose sense to mean permeability. This paper is not entirely free from this fault, and for that reason an appendix of definitions is included which may help if the exact meaning is not clear.

In order to be able to discuss the factors at work on an electrical profile, it will be necessary to outline briefly the principles on which electrical logging is based.

There are several excellent papers by Messrs. Schlumberger and Leonardon with diagrams and descriptions of circuits used, and those who have read them will realize that they have been quoted and paraphrased freely in this paper.[1, 2, 3]

Resistivity Profile.

With the exception of certain metallic ores which have the property of electronic conductivity, rocks possess only electrolytic conductivity—that is to say that while the rock itself is non-conductive, the electrolytic fluids filling the interstices can conduct an electric current. Further, the degree of conductivity is proportional to the amount of fluid in unit volume of the rock and to the amount of dissolved salts in the fluid.

Hence compact rocks having little included fluid, such as completely cemented sandstones, granites, gypsum, rock-salt and coal, show low conductivity or conversely high resistivity, whilst porous * rocks show low resistivity, provided, of course, that they are water saturated. Clearly, if they are saturated with oil, gas, pitch or absolutely fresh water, their resistivity will be high.

The degree of permeability of a rock (Appendix I) is, under these conditions, of the utmost importance.

In impermeable rocks such as shale, clay and some sandstones, the water will contain in solution the maximum of soluble material present in the rock. This solution will be chemically uniform, and the resistivity may then be a reliable characteristic of the rock itself.

However, in permeable rocks, where liquid can circulate quickly under the influence of such forces as gravity, rock pressure, gas pressure, hydrostatic head of drilling fluid, etc., the chemical characteristics of the fluid will vary appreciably, and the resistivity of the fluid in two parts of the same rock will differ with the concentration of electrolytes. In short, in permeable rocks the resistivity will reflect the character of the circulating fluids rather than of the rocks.

By circulating fluids, the fluid introduced for drilling purposes is not necessarily meant, although under prolonged conditions of high differential hydrostatic pressure, possibly with poor mud, it must be expected that the fluids contained in the rocks adjacent to the well are considerably altered by admixture with water from the drilling mud.

Measurement of Resistivity.

As is well known, a three-wire cable is lowered into the well, terminating in three electrodes spaced so as to give convenient specific values.†

One of these electrodes—let us say the primary—is put under a high electrical pressure, and forms in effect the centre of concentric spherical surfaces of equal potential.

If then a potentiometer is connected between the two secondary electrodes which lie at different distances from the source of high potential, it will show that the inner electrode is picking up a higher potential than the outer one. The difference in potential will be due to the resistivity of a hollow sphere of the earth the thickness of which is the distance between the secondary electrodes; *i.e.* about 2 feet.

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* Porous rocks here include any rock made up of grains, however small, between which there are interstices. For instance, all the shales found in the oil-fields of Trinidad. (See Appendix I.)

† It is understood that modifications of the arrangements for the recording of resistivities are now in use, but as the broad principles are, for the purposes of this paper, unchanged, it has not been considered necessary to include a description.

In practice the distance between the primary electrode and the outermost secondary is made some 25 times the diameter of the hole, and the resistivity recorded is that of a hollow sphere of earth of some 25 feet external radius and 2 feet thickness. The size of this sphere could be increased to give readings at a greater depth into the formation, but there would be an accompanying loss in selectivity, owing to the corresponding increase in the vertical height of the formation involved. It will be seen that the effect of the mud in the hole is only a slight distortion of the hollow sphere at the two points at which the hole passes through it.

Effects of Drilling Mud on Resistivity.

In considering the effect of drilling mud on the resistance of permeable rocks, the following factors have to be taken into consideration :—

1. The permeability of the rock.
2. The colloidity or wall-sealing properties of the mud.
3. The electrolytic concentration of the fluid in the rock, and of the mud.
4. The hydrostatic head of the mud, and the formation pressure.
5. The time of contact.
6. Depth.

1. *Permeability of the Rock.*—The "effective" permeability of a rock is, of course, dependent on several factors, such as the size and shape of the grains, and the diversity of size, their orientation, the degree of cementation, and the character of the enclosed fluids, *i.e.* oil, gas, water, with their different abilities to travel through and to displace each other, from capillary openings.

The degree of permeability is, moreover, subject to pressure conditions, and rocks apparently impermeable under a low differential pressure may become appreciably permeable with an increase in pressure.

An angular coarse-grained rock without cementation under given pressure conditions obviously provides the easiest passage for an invading fluid under a given greater pressure.

On the contrary, a fine- or mixed-grained rock with considerable cementation, and having such inter-connecting pore-spaces as may exist filled, say, with a viscous oil, will clearly offer considerable mechanical resistance to an invading fluid.

Hence the following remarks on the effects of mud are, of course, qualified always by the conditions of permeability, for in, say, 100 per cent. impermeable rock it is obvious that mud qualities are of no importance. For this reason interpretation of resistivity profiles should be supplemented by a study of permeability profiles.

2. *Colloidity of Mud.*—It is an established fact that a mud of poor colloidal content will fail to seal off a permeable formation, and that, further, it will lose its water to the formation while forming a porous mud pack on the wall of the hole.

This mud pack will continually increase in thickness in its effort, so to speak, to seal the permeable formation. It is sometimes the case that the critical thickness of the mud pack to effect a seal is so great as to obstruct the passage of the bit or drill-pipe, and in consequence, as the bit is run

or withdrawn or the hole is reamed, the mud pack is continually being broken off the walls. This results in further loss of water to the formation and rebuilding of the mud pack.

Thus, once the permeable formation has been exposed by drilling, a continual, though of course gradually diminishing, loss of water occurs, unless either the colloidal properties of the mud are improved, for instance, by the addition of some colloidal mineral, or the permeable formation is cased off.

The water passing through the channels in the formation will eventually drive out much of the natural fluid, and must therefore considerably modify the resistivity characteristics of the formation.

3. *Electrolytic Concentration.*—Consider the case where the salinity of the formation fluid is high, whilst that of the mud is low.

A gradual dilution of the saline rock fluid by the fresh fluid from the mud will cause a gradual lowering of conductivity, and the influence of this effect will spread further and further from the axis of the well. This explains why a second electrical survey in the same well will often show increased resistivities in water-bearing formations. (Fig. 1, Section (7).)

Conversely, if the salinity of the mud is higher than that of the formation fluid, there will be a gradually widening zone of conductive fluid in a rock the fluid of which was previously of high resistance.

4. *The differential pressure* in the formation at the wall of the hole will result in the tendency for passage of fluid either from the hole into the formation or vice versa.

Provided that the drilling mud is of good quality and of just sufficient weight to overcome the formation pressure, little fluid will pass into the formation before it is partly, at any rate, sealed off by a colloidal sheath.

In this case—and it is definitely the more usual—the resistivity of the formation fluids will not be materially affected by invading fluids of different characteristics, and a true index of the specific resistivity will be obtained. (Fig. 1, Section (9).)

Where particularly heavy mud is in use, or when the well is deep, clearly mud of better colloidal quality is necessary to effect an equally efficient seal.

Where passage of fluid is taking place from the formation into the well, a true index of resistivity will be obtained, no matter what the quality of the mud. It may be advisable to anticipate here by mentioning that reversed porosity effects will indicate when these conditions exist. (Fig. 1, Section (5).)

5. *The Time of Contact.*—This point is rather self-evident, for the mud fluid is able with the passage of time gradually to displace the formation fluid more completely and over a greater area, from permeable formations.

This statement assumes that a mud will never give a perfect seal, and while this is almost certainly true, it is in turn qualified to some extent by the factor of pressure differential. However, even if the pressure differential is nil, the effects of osmosis can probably not be ignored.

6. *Depth.*—Before leaving the subject of resistivity, mention must be made of the effects of depth, or, more properly, of temperature and pressure, both working towards the same end; *i.e.* decreasing resistivity with increasing depth.

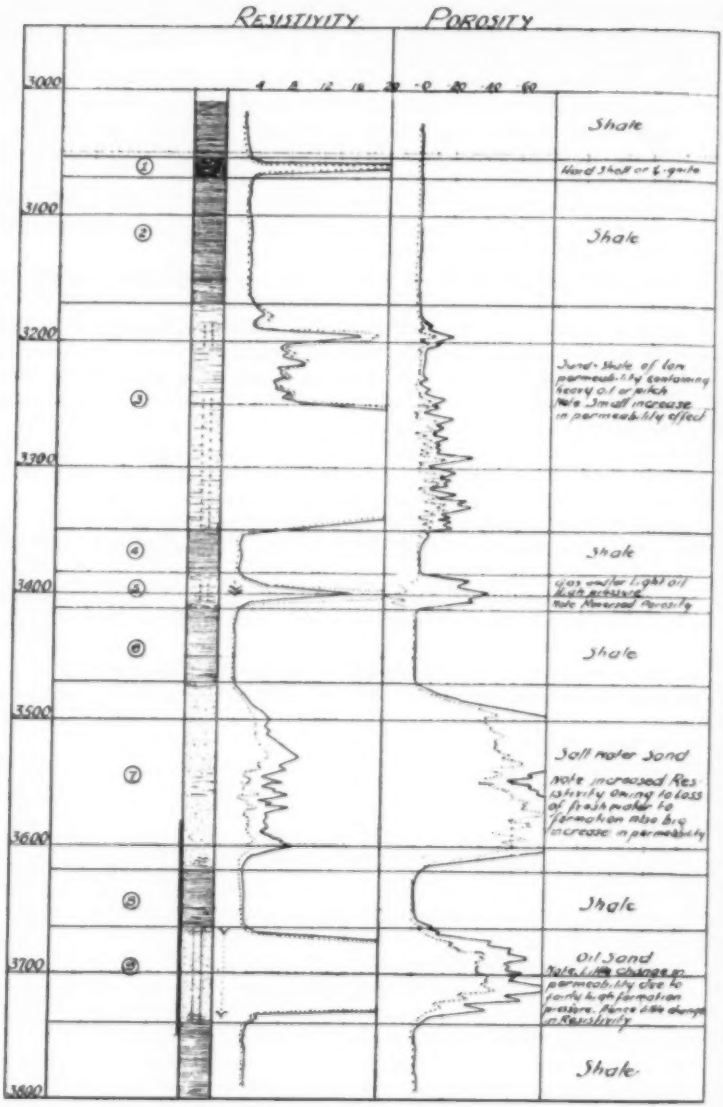

FIG. 1.

1ST RUN, DOTTED CURVE, REPRESENTS PROFILE MADE WITH GOOD LIGHT MUD.
2ND RUN, SOLID CURVE, REPRESENTS PROFILE MADE WITH POOR HEAVY MUD AT SAME ELECTROLYTIC CONCENTRATION.

The reasons for the decrease are as follows :—

1. The resistivity of an electrolyte of a given concentration decreases with temperature.
2. The percentage of dissolved salts increases with the temperature.
3. For a given formation pressure the hydrostatic head at greater depths may cause a greater loss of fluid to the formation. This, however, will not apply to impermeable rocks.

Conclusions.—From the above it can be concluded that to assign a numerical production value to a single sand or group of sands in a single well based on the specific resistivity is impossible.

On the other hand, if a series of wells be drilled to the same sand under similar conditions of mud, hydrostatic pressure, depth and time, a reasonably good forecast can be made from the basis of results from the group.[2]

From the point of view of correlation, electrical coring has established itself so firmly and successfully that it needs no defence. The resistivity profile of a well, if not always in detail, at any rate in its general characteristics is usually too distinctive for serious errors in correlation.

In the rare cases where electrical markers are so poor that there are no distinctive features either on the resistivity or on the porosity profile, it is submitted that mechanical coring would show no more, and probably considerably fewer, lithological differences. (This excepts such evidence as may be obtained from palæontological or heavy mineral evidence.)

Porosity Profiles.

Electro-Filtration Phenomena.—The value of the resistivity log is very considerably enhanced by the addition of a porosity or more correctly permeability * log, since a close examination of the two together will often show clearly points which might be overlooked or misinterpreted in either singly.

First, as to the electrical principles of the porosity log:

In 1809 Reuss found that water will move through a porous plate when an electrical potential is applied. He was followed by Quincke, who proved that the converse held true, and who applied the term "streaming potential" to the generation of electrical potentials by the passage of water through a porous layer.

This streaming potential gives rise to an electromotive force which is proportional to the pressure causing flow, and to the electrical resistivity of the fluid, and inversely proportional to the viscosity of the liquid.

By Poiseuille's law the quantity of fluid flowing through a capillary tube is proportional to the difference in pressure and inversely proportional to the viscosity.

If these two expressions are combined, it is found that the electromotive force set up by the passage of a given electrolyte is proportional to the amount of liquid which is filtering through, and to its electrical resistivity; in other words, it is a function of the permeability. This electromotive force sets up a current which flows in the same direction as the fluid.

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* See Appendix I.

Now, in the case of a well where water from the mud is filtering through the formation and pushing ahead of it the fluids of the formation, clearly an electromotive force is spontaneously generated, and a current flows in the direction of filtration; *i.e.* from the well to the formation. That is to say, that at the surface of a permeable formation the electrical pressure or potential will be a minimum, whereas at the surface of impermeable formations, where no filtration takes place, there will be no potential drop. (Fig. 1, Sections (1) and *e.g.* (2).)

The differences of potential amount often to as much as 60 millivolts, a pressure drop which is easily measurable.

Thus it will be seen that the porosity profile is perhaps even more greatly influenced by mud conditions than the resistivity profile, for porosity measurements are taken only at the wall of the hole, whilst resistivity measurements include a zone of formation extending back horizontally some 25 feet.

Before a description of the method of measurement of porosity is given, it is desired to make it very clear that whereas in the measurement of resistivity an electrical pressure is applied to the formation by means of a battery or other source of electromotive force, in the case of measurement of porosity no electric force is applied to the formation. The electric forces to be measured are spontaneously developed in the formation by electro-filtration and electro-chemical phenomena. (The latter term will be explained later.)

Measurement of Porosity.—The electro-filtration and electro-chemical differences of potential can be measured directly with a potentiometer at the surface. One of the three electrodes used for resistivity data is connected via a potentiometer to earth through an impolarizable electrode. (The reason for the latter is to avoid electro-chemical forces being set up, which would interfere with the measurements which are to be made.) Then the varying potentials at the electrode, assuming the earth connection to have zero potential, will be recorded continuously on a chart in exactly the same way as the resistivity, a drop corresponding to a permeable rock and an increase to an impermeable rock.

(The methods of recording simultaneously the resistivity and porosity profiles fall outside the scope of this paper.)

Electro-chemical Forces.—Mention was made above that the forces generated spontaneously in the rock are caused by electro-filtration and electro-chemical means, and the first has already been discussed.

Electro-chemical forces differ from electro-kinetic forces primarily in that they are of chemical and not of dynamic origin. When two phases are brought into contact, there may exist a difference in potential between them. Common cases are between metals and gases, and metals and solutions, between solutions of different electrolytes, and between solutions of the same electrolyte but of different concentrations.

Probably the best-known application of electro-chemical potentials is in galvanic cells, and batteries. If a rod of zinc and a rod of copper or carbon are dipped into a solution of dilute sulphuric acid, a current is found to flow from the copper to the zinc.

Further, although the amount of the current will vary according to the size of the rods, the potential difference will be a constant, depending on

the materials involved in the reaction. Consequently, variations in potential will reflect the properties of the materials under investigation.

In exactly the same way, electro-chemical forces are caused by reactions between the mud fluids and rocks containing fluids of different chemical compositions or concentrations. In general, these currents are much smaller than those caused by electro-filtration, but in contradistinction to electro-filtration currents, no fluid travel is necessary for their generation, which is entirely a contact phenomenon.

If, for instance, a strong salt-water sand is exposed in a well, containing non-saline mud fluid, then, even where there is no differential pressure, an electro-motive force is set up in the direction from the non-saline fluid to the saline, that is, from the hole into the formation, and a current will flow in this direction.

Conversely, if a salt-water mud were being used in a well which penetrated a fresh-water sand, a current would flow from the formation into the well.

Considering the case where a well using non-saline mud penetrates a low-pressure salt-water sand, a porosity diagram will show the effects of the two electrical forces superimposed, for the electro-filtration current will flow from the hole into the formation; *i.e.* in the direction of filtration, whilst the electro-chemical current will also flow from the hole into the formation; *i.e.* in the direction of greater concentration.

The electro-filtration effects are usually greater than the electro-chemical, and in the majority of cases discrimination, even if possible, would serve no useful purpose, for the porosity log in any case gives not the true pore space/volume ratio of the rock, but the reaction of the rock to the invasion of fluid under existing well conditions.

In particular instances, however, electro-chemical phenomena may become too important to ignore, as when the salinity of the formation fluid is considerably higher than that of the mud, or vice versa.

In the first case the electro-chemical and electro-filtration effects will be superimposed, whilst in the second case they will be opposed. Clearly, however, if the formation pressure is greater than the hydrostatic pressure, the converse is the case.

To reiterate, a striking difference is found between electro-chemical and electro-filtration phenomena, for the former are unaffected by differential pressures, whilst the latter are almost entirely dependent on them.

In point of fact, advantage has been taken of this feature in instances where electro-chemical effects are negligible in the measurement of formation pressures by varying the hydrostatic head, and recording the corresponding porosity effects. The value of the formation pressure can then be calculated quite simply, but this branch of the subject falls outside the scope of this paper.[1, 4]

Effect of Mud on Porosity.

1. *Colloidity.*—As was the case with the resistivity log, so also it is found in the porosity log that the quality of the mud will affect the numerical values obtained.

A mud of poor colloidal properties will allow a continual and free filtration

of fluid into a permeable formation, and, as has been seen, the electro-motive force generated is proportional to the amount of liquid which is filtering through in any instant of time.

A good mud will lessen the amount of filtration, and a lower porosity figure will be obtained, for an identical formation. This might appear to be a considerable drawback, but is not so serious as might be imagined. To begin with, the same mud is against the formation all through the hole, and the profile will therefore tend as a whole to be intensified or moderated.

Secondly, for a given area or field, where mud is usually obtained from the same source, the quality of the mud as regards sealing will not vary very much, except in peculiar circumstances—for instance, where there is a strong local salt-water sand, or where the mud has been chemically treated, or contaminated by cement. In such cases, the porosity log would be examined with due attention to the disturbing factors.

2. *Differential Pressure.*—The differential pressure between the mud and the formation fluid due to the specific gravity and the depth head of mud, influences the porosity figures obtained, since porosity is proportional to the quantity of fluid filtering through. In some cases there may be no differential pressure and no porosity effects may be seen, although the formation may be highly permeable.* In other cases, again, reversed porosity effects may be recorded, indicating that at the time the profile is made fluids are actually leaving the formation and coming into the well. (Fig. 1, Section (5).)

Here it may be as well to point out that water will more easily invade water-wet capillaries than oil-wet capillaries. This is one reason why water sands usually show higher porosities than oil sands. (Fig. 1, Sections (7) and (9).)

3. *Time of Contact.*—The longer the time of contact of a given mud with the formation, the lower falls the porosity. This is fairly clear, when it is considered that capillary spaces will gradually become choked and the quantity of fluid being filtered will gradually dimínish.

Cases of this can frequently be seen where the same well is electrically cored twice in the same mud, where formations at the second run show considerably reduced electro-filtration effects. Particularly is this noticeable when there has been serious loss of mud, either as mud if such a thing occurs on an appreciable scale, or as water from the mud.

When only one electrical survey is made, and mud has been lost in considerable amounts, it must be borne in mind that a porous formation in the well somewhere has absorbed a considerable quantity of drilling fluid, and its porosity may have been considerably reduced.

This point is important, as in most cases of lost circulation, in country where cavities are exceptional, a water sand is probably the thief. A study of the resistivity profile will assist in this case.

4. *Salinity of Mud.*—Finally, there is the influence of the salinity of the mud. This has already been discussed in its application to "electro-chemical forces," and will not be further enlarged upon, except to point out that the higher the salinity of the mud compared to the formation fluid, the lower will be the electro-filtration effect and the stronger will be the

* This statement does not take into consideration any electro-chemical phenomena.

opposing electro-chemical effect. In fact, if the salinity of the mud exceeds that of the formation fluids, reversed porosity effects may be observed.[2]

Finally, where the salinity of the formation fluids and the mud are the same, no electro-chemical effects will occur, and under these conditions the profile will give a true index of the permeability of the formation.

Interpretation of Combined Logs.

Certain features of the logs obtained by electrical coring will, it is hoped, be explainable by reference to the foregoing. As a general basis of interpretation, the list in Appendix II and the hypothetical Well Log (Fig. 1) may be helpful.

It must be remembered, however, that any well profile should be studied as a whole, with due attention to other wells in the immediate neighbourhood, where formation conditions are similar, and that any distracting features, such as the hydrostatic head of the mud, the salinity, and the colloidity of the mud, and the time of contact, have all had their effect on the electrical log, and cannot be ignored, if a correct interpretation is being attempted.

Given experience of the effect of these influences at increasingly greater depths based on combined mechanical and electrical coring, the writer feels that the exploitation geologist, in fields even as lithologically variable as in Trinidad, will be able at any rate to state with certainty whether a formation is worth testing, and whether results are liable to be good, bad or indifferent.

Finally the author wishes to acknowledge his indebtedness to Mr. Bayle for many helpful suggestions and to Messrs. Trinidad Leaseholds Ltd. for permission to present this paper.

Appendix I.

"The *absolute porosity* is the percentage relation of the volume of all pores, sealed and interconnected, of a body to its bulk or apparent volume."

"The *effective porosity* is the percentage relation of all interconnected pores of a body to its bulk or apparent volume."

"*Permeability* is the property of a solid which makes possible the transport or conveyance of fluids through it."[5]

Permeability varies therefore with the type of flow, the direction of flow relative to bedding planes, the pressure causing flow and the shape and size of the capillary openings, and consequently two rocks having the same effective porosity may have different permeabilities.

Appendix II.

High Resistivity, Low Porosity (Fig. 1, Sections (1) and (3)).—Indicates compact rocks, such as granites, quartzite, gypsum. Also sands containing very heavy oil or pitch, or fresh water at shallow depths. Poor in water and saline material. Might give small production of heavy oil. Also suggestive of good mud. Possibility of porosity being part way to reversal.

A change of mud-weight or salinity and a second profile would assist, if in doubt.

High Resistivity, High Porosity.—Indicates uncompacted rocks containing lighter oils or gas. Good production possibilities. If porosity is very high, suggestive of depleted sands. Also suggestive of poor mud, but not if resistivity is really high.

Low Resistivity, Low Porosity (Fig. 1, Sections (2), (4), (6), etc.).—Indicates compact rocks such as shales with high saline content, rich in trapped water, typical of Trinidad shales.

Low Resistivity, High Porosity (Fig. 1, Section (7)).—Indicates salt water-bearing uncompacted rocks. Also suggestive of poor quality mud. In very exceptional cases may indicate oil sands from which low-viscosity light oils have been driven out of zone of electrical influence, by saline mud fluid.

References.

1 "Electrical Coring: A Method of Determining Bottom Hole Data by Electrical Measurements." C. and M. Schlumberger and E. G. Leonardon, A.I.M.M.E. Technical Publication No. 462.

2 "A New Contribution to Subsurface Studies by Means of Electrical Measurements in Drill Holes." C. and M. Schlumberger and E. G. Leonardon, A.I.M.M.E. Technical Publication No. 503.

3 "Electrical Coring: Its Application to Rumania in 1931–32." C. and M. Schlumberger, *Proc. World Petr. Congr.*, 1933, **1**, 341.

4 "Deep Borehole Surveys and Problems." Haddock.

5 "Physical Tests and Properties of Oil and Gas Sands." Fancher, Lewis, and Barnes, *Proc. World Petr. Congr.*, 1933, **1**, 322.

DISCUSSION.

Dr. H. G. Kugler congratulated the author on his lucid explanations of the main phenomena controlling the process of electrical coring.

During the 2½ years of routine application of this geophysical survey method on almost every well drilled by oil companies in Trinidad, sufficient information was obtained to prove the great value of the electrical surveys of wells. It is not only valuable for the purpose of correlation of formations, but also for detecting the entry of water (water-witch), deviation of boreholes and temperature measurements.

The electrical determination of the direction of the dip of formation will undoubtedly be applied in all future exploration wells which penetrate unconformities. Electrical determinations of the height of the annulus of cement outside casing is possible, and may soon be a matter of routine.

Electrical coring was greatly improved between March 1929, when he had an opportunity to see the early resistivity logs of the Caribbean Petroleum Company at Maracaibo, and to-day, when certain companies of the Maracaibo Lake district claim to be able to forecast the production from the order of magnitude of the resistivity and permeability log.

The author clearly demonstrated that no comparable specific factor for any formation could be measured without taking into consideration the nature of the drilling mud. In Trinidad it was noted that high-pressure fields offer more accurate results than those with prevailing low-pressure reservoirs. A field in the south-west of Trinidad was an outstanding example of a low-pressure area where the early electric logs

led to misinterpretation. In that field production is derived from Miocene sandstones. They attain a thickness of more than 3000 feet, and contain oil and salt water interdigitated in the lower part of the monoclinal structure. During drilling the formation absorbs considerable amounts of fresh water from ordinary drilling mud, thus obliterating the low salt-water permeability profiles by high fresh-water peaks which could be mistaken for oil sands. Introduction of salt water followed by a further electrical survey permitted the location of the probable oil sands, which could then be separated and produced. Recently the use of the original arrangement of the electrodes as described by the author was used to allow greater lateral penetration, with the result that oil sands showed up more distinctly from salt-water sands contaminated by fresh water. But, as the author stated, there was an accompanying loss of selectivity.

In order to overcome those and other difficulties, one might visualize a time when, in certain fields, a synthetic drilling mud completely devoid of any free water will be used.

Dr. Kugler said it was gratifying to see that the study of the physical properties of reservoir rocks was receiving more and more attention on the part of the scientifically minded petroleum engineer.

Mr. G. H. Scott said the paper clearly showed the effect of varying factors on the normal resistivity and porosity profile of the electrical log.

He had heard it claimed in the early days of electrical coring that one could foretell the potential productivity of a well from a study of the porosity and resistivity log, and he had then thought, as a layman on the subject, that such deductions were fraught with serious pitfalls for the budding exploitation geologist. He considered, therefore, that the paper showed in a very clear manner that one had to be in possession of a mass of ancillary data before one could even hope to estimate productivity values. He was interested to see that the author favours a combination of mechanical coring with electrical coring in order to correlate electrical characteristics with the lithological. That was the speaker's idea of the optimum. He would prefer to see every hole cored and electrically surveyed to give the maximum data. He was sure that he would meet with the criticism on the question of expense; he was not going to join issue on that question, but he did feel that the amount so expended would be justified, as one was sure to get the maximum information from the drilling of a well. Mechanical coring gave information that the electrical log could not give, and the converse was also true to a lesser degree. He thought, therefore, that a combination of both, in any case in the early stages of development of any field, was essential under operating conditions.

Mr. J. L. Harris said that, from what the author had stated, it was very obvious that mud did have a great effect on the profiles which were recorded on the resistivity log and the S.P. log in the Schlumberger core.

He thought from that it should be possible if one took a sufficient number of those electrical surveys to modify the log thus obtained under non-standard conditions to standard conditions. He quite agreed with Mr. Scott that one could not get away from physical coring in a well, but he thought that possibly, as physical coring was more expensive than electrical

coring, electrical coring might be regarded as standard practice. It was as much a truism to assert that if a well was worth drilling it was worth an electrical survey, as to insist that if a well was worth producing it was worth a special tank to measure the production. The more results obtained by electrical surveys of wells (taking due note of the mud characteristics in every well) the nearer they would be to forecast the productivity of a well from the S.P. and resistivity logs obtained.

Mr. G. W. Halse said the author had brought out very clearly the immense importance of the relation between the fluid contents of the strata and their electrical reaction. This implies that in certain circumstances electrical logs would be expected to show considerable indifference to lithological properties. As an instance of this, Mr. Halse cited the case of a group of wells in Venezuela, which passed through a strong angular unconformity. Above the unconformity were mottled clays and shales of Lower Miocene or Oligocene age. These rested unconformably on indurated brittle shales with very thin glauconitic calcareous sand bands of Eocene age. Lithologically, the change was most striking and unmistakable, and yet, if there were no sands in the mottled clays, the electric log always went through the unconformity without showing any change. This was, no doubt, a comparatively unusual set of conditions, but it was one in which some mechanical coring was indispensable. Oil sands, of course, were registered perfectly satisfactorily without exception.

Mr. C. E. Capito said that, before reading the paper, he had been laboriously going through the Schlumberger logs in the Petroleum Office trying to correlate porosity or resistivity with production. Curves showing maximum resistivity against production per mean ohm over different periods, the wells in each area having their separate curves, showed nothing that would correlate at all.

The author states: "In rare cases where electrical markers are so poor that there are no distinctive features either on the resistivity or on the porosity profile it is submitted that mechanical coring would show no more and probably fewer lithological differences." The speaker submitted that mechanical coring would definitely show dips, and whereas a Schlumberger log might show an 80-feet sand, if mechanical coring had been undertaken, the dips might have proved the sand to be quite a thin one.

Mr. C. A. Moon said that the point which impressed him most was that although electrical coring did give a very complete record of the hole, it seemed that to be able to interpret the log properly, it was more than ever necessary to keep accurate well records. The recording of the weight of mud, its properties, conditions and its salinity; the static gradient due to the mud, checks on the amount of fluid absorbed by the well, and the points at which the well did take fluid were essential.

The actual taking of the electric log was very rapid, and involved running heavy plummets into the well, occupying half an hour to 2 hours, but it takes weeks, perhaps months, to collect the other essential data for the proper interpretation of the electric log.

On the question of mechanical coring being done as well as electrical coring, he thought it excellent to have both records, but that, on occasions,

one would conflict with the other. He suggested that if the geological staff were locked in one room with their cores, and those responsible for drilling, with their collected data, were put in another room with the Schlumberger logs, different values would be given to each log. He thought that they would get more useful results from the Schlumberger logs than from continuously cored logs in Trinidad.

Mr. P. Bayle wished to clear up one point as to the exact meaning of the so-called " Porosity Log."

He had recently received some new ideas dealing with the theory of the sealing-off action of drilling mud. From research work made on this subject the following important results have been obtained :

First, if pure water is percolating through a sand, the quantity of water " Q " passing per unit of time increases as the " effective porosity " of the sand increases. It is assumed that " Q " represents what the author terms the " effective permeability " of the sand.

Secondly, if clay mud (even poorly colloidal) is percolating through a porous sand, the quantity of mud passing per unit of time will tend very quickly to a low and uniform value, a sort of asymptotic limit, which would not depend at all on the " effective porosity " of the sand. Clearly, this limit would be approached quicker, if one deals with a very colloidal mud, called a good mud by the author. This asymptotic limit being assured leads to this important conclusion :

The quantity of fluid percolating per unit of time depends only on the differential pressure causing the flow—i.e. *it is directly proportional to this differential pressure.*

In other words, after a very short time " the effective permeability " as defined by the author would be apparently identical for the varying sands, since this permeability should be considered only in the immediate vicinity of the walls of the hole. In other words, the factor " permeability " which enters the Poiseuille formulæ refers to the mud pack, and not to the virgin sand.

According to this hypothesis, the porosity log merely shows the variation of the differential pressure opposite every porous layer, and does not give much information as to the " effective permeability " of each sand.

Needless to say, this conclusion supposes that no electro-chemical effect is taking place.

Thus, even if only the effect of electro-filtration exists, it follows, from the foregoing, that the term " permeability log " suggested by the author would still be inaccurate.

To be completely non-committal it is suggested that the generic term S.P. log be used—S.P. means spontaneous polarization.

The S.P. effect is actually what is recorded, whatever the cause might be. It represents the total amount of millivolts obtained " spontaneously " on the measuring electrode.

The correct interpretation of the S.P. log is the precise allocation of the influence due to the different factors :

" Effective permeability " of the sand ;
" the differential pressure " ;
" the electro-chemical actions," etc.

Naturally, as the author has concluded, a perfect knowledge of the mud characteristics is necessary to achieve an accurate interpretation.

Mr. H. C. H. Thomas, in reply, thanked those who had taken part in the discussion for their comments.

Dr. Kulger had directed attention to the very wide range of data that could be obtained by electrical means in a well, especially with regard to the location of salt water, determination of the direction of dips, and deviation surveys.

He referred to the greatly advanced technique which had been developed during the last few years as the application of electrical methods grew more general.

With regard to the question of muds devoid of free water, the author had seen these mentioned in several recent articles on mud treatment, but found difficulty in understanding what exactly was meant. He took it that a mud of high colloidal content which sealed the formation without appreciable loss of water was what was implied. He could not see how a mud could be made in which all the water existed in the combined state—that is, in either physical or chemical combination.

He had always considered that the bulk of the water acted as a free vehicle, to the suspended particles, whether of colloidal size or greater.

Mr. Scott stressed the point that a combination of electrical and mechanical coring was the ideal, although he anticipated criticism on the grounds of expense.

While the author agreed that the combination was essential in the early stages of development, he thought, with Mr. Bayle, that during exploitation the mechanical coring of an occasional key well or outstepping well, as is being carried out in some Venezuelan fields, would be sufficient to give such necessary data as could be obtained only from visual examination of the formations.

In this he was influenced by the question of cost, to which Mr. Harris had also referred, and with those remarks he was in entire agreement.

Mr. Halse has quoted an instance where electrical coring failed to differentiate between two formations separated by an angular unconformity, although they were of markedly different lithological character when examined by mechanical coring. The author agreed that where electrical characteristics were similar, electrical coring could not discriminate. This point supported Mr. Scott's argument in favour of a combination of both methods of coring.

The author thanked Mr. Capito for his remarks, and was glad to feel that his paper had been of assistance to one who had the opportunity of studying electrical logs from so many different fields in Trinidad.

Mr. Moon suggested that a record should be kept of the absorption of fluid by the well. The author was fully in agreement where such absorption was abnormal. He knew, in fact, of a case in which all water added to the mud stream was metered, and he thought that this was a definite step towards the better interpretation of the electrical log.

Mr. Moon raised the point that rather different results might be obtained from an independent study of electrical and mechanical core logs. The author agreed that this was possible, and for that reason he and other

speakers had recommended the combination of both methods in difficult country. Were he to be asked to state a preference for either form of log in a proven field, taking into account the higher cost of mechanical coring and the various difficulties involved, he would tend to prefer the electrical method.

Mr. Bayle made the interesting suggestion that it was the permeability of the mud sheath rather than of the formation which controlled the rate of filtration.

The theory was new to the author, who could have said rather that the rate of filtration was determined by the clogged area immediately behind the mud sheath. However, he agreed with Mr. Bayle that the term permeability log might be little preferable to the term " porosity " log, and he thought that " S.P." or " spontaneous polarization log " would not only give the truer picture, but would also help to remove misconceptions as to the meaning of the values obtained.

On the motion of the **Chairman**, a vote of thanks was accorded to the author and to their hosts, the President and Members of the Apex Club, for the use of the building.

SOME THERMAL REACTIONS OF HYDROCARBON GASES.*

By F. I. L. Lawrence.†

Synopsis.

In this review of the literature, some thermal reactions of hydrocarbon gases, of from two to four carbon atoms inclusive, are discussed. The mechanism of the reaction forming aromatics from normally gaseous paraffins between 600° and 750° C. is discussed, and the path found to be

Paraffin → Olefin + H_2
Olefin + lower molecular weight paraffin
Olefin + Olefin → diolefin (4 or more C atoms) + H_2
Diolefin + Olefin → *cyclo*-olefin + H_2
cyclo-Olefin → *cyclo*diolefin + H_2
Aromatic + $2H_2$.

The thermal decomposition of both paraffins and olefins is considered empirically and theoretically. Rupture of the C–C bond at every conceivable place seems possible, in addition to dehydrogenation to the corresponding olefin. The formation of polymers, or miscellaneous liquid reaction products, at elevated temperatures is reviewed. Liquid yields up to 25 per cent. by weight have been obtained by the thermal decomposition of paraffins and up to 40 per cent. by weight by the pyrolysis of olefins. The practical ultimate yield that may be obtained from a gas containing 50 per cent. olefins and 50 per cent. paraffins appears to be of the order of 50 per cent. by weight of liquid products.

The thermal reactions of hydrogen with hydrocarbons appear to be a direct factor in lowering the ultimate yield of liquid products. Some surfaces, particularly iron, nickel, and graphitic carbon, promote the decomposition of the gaseous hydrocarbons into their elements either directly or indirectly. Some types of processes with a high liquid yield are considered.

I. INTRODUCTION.

The investigations of the pyrolysis of hydrocarbons have become increasingly frequent since the first one was made in 1792 by Murdock. The earlier investigations were sparse and meagre, whereas to-day they are carried on simultaneously by many in great detail; because of which this review will be limited to that branch of the art which concerns those hydrocarbons of less than 5 carbon atoms, excepting methane. The reports of investigations made before 1915 were not examined by the author except in a few cases. Those data, as well as the results of many investigations published from 1915 to 1929, have been rather completely covered in several earlier reviews, notable among which are those by

* Paper received March 9th, 1935.
† Atlantic Refining Co., Philadelphia, Pa., U.S.A.

Egloff, Schad and Lowry,[11, 12] Hurd,[28] Hague and Wheeler,[26] Williams-Gardner,[66] Stanley,[61] and Dunstan, Hague and Wheeler.[13]

There were many early investigators,* who were hampered by lack of the equipment which is at the disposal of the modern investigator, particularly analytical fractionating columns, improved analytical apparatus, and new materials for apparatus, by means of which it is now possible to obtain more complete data. In considering the reported results, more weight must be given to those completed in the last few years, because of these more accurate analytical results.

The confusion observed in this field of scientific investigation has been caused by the publication of many apparently contradictory results, which were undoubtedly obtained in good faith by the authors, but the error of which lay in not completely understanding the interdependence of the large number of variables involved. The most important of these variables is the temperature of the reacting gases, by varying which the speed of the reaction may be controlled from zero per cent. reaction to practically instantaneous formation of carbon. The rate of decomposition at a given temperature increases regularly with the molecular weight of a hydrocarbon series. The effect of time of reaction is also largely responsible not only for the observed extent of decomposition, but also for the character of the products obtained. Unfortunately, this fact was not realized as being of more than minor importance until quite recently. Although pressure has some effect apart from its effect on time, very little is known on the subject except for the obvious influence on olefin polymerization at comparatively low temperatures. One of the less important factors affecting the pyrolysis of the gaseous hydrocarbons is the surface of the reaction vessel. Some materials such as silica are non-catalytic, whilst others such as monel metal are very active, and cause decomposition to carbon, hydrogen and possibly methane. Unless otherwise noted, all published results discussed in this paper have been carried out in reaction vessels with an inactive surface such as glass or silica. The presence of some diluent gases such as oxygen and hydrogen has been found to exert a marked effect on the thermal reaction of gaseous hydrocarbons, whilst nitrogen has no apparent effect other than that of an inert diluent.

In the thermal reactions of gaseous hydrocarbons, it appears to be a fact that they are nearly all unstable with respect to their elements. Although the ultimate products of reaction may be carbon and hydrogen, it is the mechanism of the reaction which is of interest, whereby as the reaction progresses many more stable products are continuously being formed from less stable ones. Since each investigator was interested in a particular stage of this process, it is no wonder that apparently contradictory results have been obtained simply because of the large number of variables involved. It is therefore necessary, in correlating the results of various investigators, to have a knowledge of these variables.

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* Murdock, 1792; Henri, 1805–21; Dalton, 1809; Berthelot, 1863–70; Thorpe and Young, 1871–73; Armstrong and Miller, 1887; Jacobsen, 1877; Norton and Andrews, 1886; Day, 1886; Norton and Noyes, 1886; Lewes, 1892–95; Doorkovitch, 1893; Haber, 1896; Worstall and Burwell, 1897; Collie, 1906; Kutznlozon, 1907; Bone, 1904; Pring, 1911; Ipatiev, 1911; Staudinger, Eadle and Herold, 1913; Jones, 1915.

II. FORMATION OF AROMATIC POLYMERS FROM GASEOUS PARAFFINS AND OLEFINS.

Gaseous Paraffins $\longrightarrow$ Aromatic Polymers.

One of the first theories of the mechanism of this reaction was evolved by Berthelot,[2] who passed C_2H_4 through a red-hot tube and obtained benzene, naphthalene, anthracene and other aromatics. He believed that the ethylene formed acetylene, which subsequently polymerized to benzene which was in this way formed from hydrocarbons with the same carbon-hydrogen ratio as benzene. His theory was corroborated by Lowes [40] and partly by Bone and Coward.[4]

It appears to the author that Groll,[23] a modern exponent of the acetylene theory, placed too much emphasis on the gross effect taking place during pyrolysis, and was probably misled thereby. He assumed that the divalent radicals, R—C=CH and HC=CH (" nascent acetylene "), were polymerized to aromatics more rapidly than the formation of acetylene hydrocarbons could take place. The author believes that if this assumption were true it should have been possible to determine the acetylene analytically. Although a number of investigators [12, 27] have examined their reaction products for acetylene, it has not as yet been found in appreciable quantities even by Groll, who apparently made no attempt to separate CO_2 from it.

Haber [24] and other earlier workers, when they were unable to find appreciable quantities of acetylene, looked with distrust on the theory of Berthelot. More recent investigations have shown the earlier methods for the determination of acetylene, in the presence of ethylene, to be misleading.

Jones [37] in 1915 introduced the concept of the formation of benzene by dehydrogenation of *cyclo*-olefins. A year or so later, Zanetti [67] postulated that aromatics were formed from hydrocarbons with a lower carbon–hydrogen ratio than benzene. Davidson [12] in 1918 found quantities of butadiene while pyrolyzing natural gas condensate in copper tubes. He could detect no acetylene in the products, except when it was charged to the reaction tube with the gas under treatment, in which case traces of quantities as small as 0·1 or 0·5 per cent. of acetylene could be detected. Davidson coupled his work with that of Jones, and suggested the following reactions for the formation of benzene :—

$$2C_2H_4 \longrightarrow C_4H_6 + H_2$$
$$C_4H_6 + C_2H_4 \longrightarrow \textit{cyclo}\text{hexene}$$
$$\textit{cyclo}\text{Hexene} \longrightarrow \text{benzene} + 2H_2$$

Davidson thought the existence of the *cyclo*hexene was probably temporary, which opinion has been substantiated by contemporary workers.

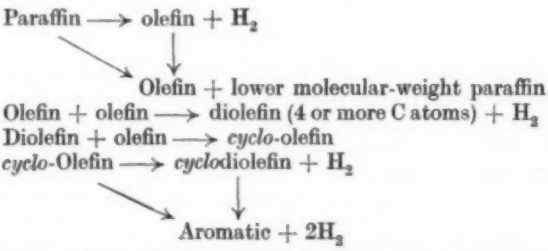
Hague and Wheeler,[27] at Sheffield University, showed that acetylene decomposed more rapidly than ethylene at temperatures at which aromatics were formed. Wheeler and Wood [65] were able to polymerize ethylene and butadiene in equimolecular proportions under conditions where ethylene alone would not polymerize. The polymer was mainly *cyclo*hexene. They then treated *cyclo*hexene at 700° C. and obtained 25 per cent. benzene,

21 per cent. tar, and quantities of ethylene and butadiene. Their conclusion was that the path followed was essentially that indicated by Davidson's work. In addition, their experimental accuracy was of a higher order than his.

Shortly after this, there appeared a notable group of papers published by investigators at the Massachusetts Institute of Technology. This work, particularly that of Schneider and Frolich,[60] agreed very well with the work carried on at Sheffield University. Schneider and Frolich, in investigating the thermal decomposition of propane with various times of contact, obtained more butadiene from ethylene than from propylene. Their method was to obtain various percentages of cracking by varying the time of contact under fixed conditions. Plotting mols of reactants per 100 mols cracked versus time of contact, the plotted data could be extrapolated to zero per cent. reaction. The actual measurements were carried out in some cases as low as 2 to 3 per cent. of cracking. As Hurd and Eilers[30] have pointed out, this method is open to the objection that stable secondary reaction products appear to be primary reaction products, but, when used with discretion, the method is useful in research. From these experiments on propane and propylene, Schneider and Frolich concluded that ethylene was the starting point in the synthesis of aromatics. They followed the reaction stepwise, and obtained first at 725° C. and 1/5 atm. fourteen times as much butadiene as butylene in the pyrolysis of ethylene. Their data indicate butadiene and hydrogen to be nearly 80 per cent. of the primary reaction products of ethylene. On examining the data, it appears that butylene may be formed on impact, and the molecule of butylene thus formed has so much energy that it simultaneously decomposes to butadiene and hydrogen. The reason for this supposition will be discussed in more detail in Section III, Part B.

These two investigators[60] next heated mixtures of 10 per cent. butadiene and 90 per cent. ethylene. They found the major primary products to be benzene and *cyclo*hexadiene in the ratio of 2 : 1 at 725° C. and 1/5 atm. pressure. By this series of experiments they may not have shown what the primary products of the reaction were, but they have demonstrated what the effective products of the primary reaction were in each case.

It can now be stated that the theory of Berthelot has been disproved for the region 600–750° C., and instead there has evolved a mechanism for the formation of aromatics which is essentially this :


Paraffin ⟶ olefin + H_2
Olefin + lower molecular-weight paraffin
Olefin + olefin ⟶ diolefin (4 or more C atoms) + H_2
Diolefin + olefin ⟶ *cyclo*-olefin
cyclo-Olefin ⟶ *cyclo*diolefin + H_2
Aromatic + $2H_2$

In the generalized equation above, the reaction between two olefins to form a diolefin is not limited to ethylene. The results of an unpublished

investigation carried out in the laboratories of this Company indicate that, under varied conditions of pyrolysis of refinery gas, particularly under pressure, benzene is not the only product formed. Very appreciable quantities of mono-, di-, and tri-carbon atom substituted aromatics are formed. It is interesting that under most conditions the quantity of substituted aromatics obtained is larger than the quantity of benzene, which is contrary to some reports in the literature. These results may be explained as follows: $2C_3H_6 \longrightarrow CH_3—CH{=}CH—CH{=}CH—CH_3$. The diolefins so formed may react further with an olefin to form substituted cyclics by ring closure.

Frey and Hepp,[18] on exhaustively analysing the products of cracking of butane at 850° C. and atmospheric pressure with a contact time of 0·9 second, found the following compounds in the fraction from propane up, which analysis is typical of many reported in the literature at atmospheric pressure.

Product.	Per cent. by Weight.
Propylene	3
Butane	5
Butadiene	4
Pentenes	1
*cyclo*Pentadiene	6
Hexadiene	1
Benzene	61·1
(Intermediate)	0·9
Toluene	9·85
(Intermediate)	0·15
Xylene plus Styrene	8·0

III. THERMAL DECOMPOSITION OF C_2, C_3 AND C_4 HYDROCARBONS.

There are two methods of approach to this phase of the subject. When the first, or empirical, method is used, the products of decomposition are isolated and an equation is written to conform with the findings. The subject is approached by the second or theoretical method through theoretical chemistry in such a manner that class reactions may be predicted from a relatively small amount of direct experimental data. Data obtained by each of these methods will be considered in some detail.

A. Empirical Method.

Until quite recently this has been the field in which most investigators have been working. A large amount of work has been completed, much of poor quality, because the investigators either made assumptions which were not valid, neglected to control certain variables, or did not have adequate analytical equipment. In most cases where carbon and hydrogen were reported as products of the decomposition of gaseous hydrocarbons, they were probably secondary products of decomposition, and not primary products. The investigators made this statement based on the fact that they found them under their experimental conditions, which generally included an enormously long reaction time. The mode of carbon formation

between 600° and 750° C. is probably through the collection of polymerized material on the surface of the reaction chamber, with subsequent further polymerization and dehydrogenation over a protracted period until nothing remains but a carbon skeleton. The mode of carbon formation from, and dehydrogenation of, hydrocarbon gases in contact with finely-divided nickel or similar materials has apparently never been satisfactorily explained. The design of the reaction vessels used is an important factor in determining the total yield of olefins from paraffins, as Cambron and Bayley[10] have shown that under conditions of turbulent flow higher rates of conversion of the lower paraffins to olefins are possible than with streamline flow. These data indicate the necessity for revision of some of the conclusions reached by various earlier workers.

Table I lists the gaseous hydrocarbons, which are discussed in the following section, together with the primary products found when they were heated to the temperature shown.

TABLE I.

Effective Primary Products of Pyrolysis.

Hydrocarbon.	Temp. (° C.).	Pressure (atm.).	Products.
Ethane . .	to 750	1	$C_2H_4 + H_2$, 100%.
Propane . .	650	1	$C_3H_6 + H_2$, 50%; $C_2H_4 + CH_4$, 38%; C_2H_6, 10%.
Butane . .	600–650	1	$C_3H_6 + CH_4$, 48%; $C_2H_4 + C_2H_6$, 35%; $C_4H_8 + H_2$, 15%.
*iso*Butane .	600–650	1	*iso*-$C_4H_8 + H_2$, 63%; $C_3H_6 + CH_4$, 35%; C_2H_6, 2%.
Ethylene .	725	0·2	$C_4H_6 + H_2$, 70%; C_3H_8, 15%.
Propylene .	725	0·2	$C_4H_8 + C_2H_4$, 50%; C_5 and C_6 olefins, 30%; CH_4, C_3H_8, H_2, C_4H_6.
Butylenes * .	600–900	1	CH_4, C_2H_4, C_3H_6, C_4H_6, and H_2, also polymers.
*iso*Butylene * .	600–700	1	Polymerization (50%), also CH_4 and H_2.

* The products of the butylenes and *iso*butylenes are not necessarily effective primary products.

1. *Thermal Decomposition of Paraffins.*

Ethane.—Frey and Smith [21] found at 575° C. and atmospheric pressure that the decomposition of ethane was a unimolecular reaction and could be represented as :—

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

They found this to be the only reaction of any consequence taking place during the first part of the decomposition. Marek and McCluer,[41] on the basis of their experiments to determine the reaction velocity constant of ethane, found at short times of contact at temperatures below 700° C., that ethane decomposed predominantly to ethylene and hydrogen, and secondary reactions, such as polymerization and demethanization of ethylene, were negligible.

Hague and Wheeler [25] have decomposed ethane at various temperatures. Calculations made by the author from their data indicate that at 700° C. 90 per cent. of the C_2H_6 decomposed appeared in the products as ethylene.

Cambron[9] found that 90 per cent. of the ethane which decomposed did so according to the equation

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

when ethane was passed through a 3·2-cm. water-cooled reaction tube heated by a concentric carbon rod at a temperature of 989° C. An ethylene yield of 50·5 per cent. by volume was obtained. There appears to be no question of C_2H_4 and H_2 being the primary decomposition products of the cracking of ethane.

Propane.—The best data on the decomposition of propane to primary products have been obtained by Schneider and Frolich.[60] The method used has already been described. They obtained as primary decomposition products of propane, when calculated to zero per cent. change, the following compounds :—

650° C. . .	$C_3H_6 + H_2 = 50\%$	$C_2H_4 + CH_4 = 38\%$	$C_2H_6 = 10\%$
725° C. . .	$C_3H_6 + H_2 = 43\%$	$C_2H_4 + CH_4 = 48\%$	$C_2H_6 = 8\%$

It may be noted here that the drift of the reaction with increasing temperature to increasing amounts of ethylene plus methane should not be taken too seriously, inasmuch as the data at 725° C. have been extrapolated over a wide range (from 20 per cent. to 0 per cent. decomposed). These data indicated ethane to be one of the primary products of decomposition, an explanation for which will be discussed in Section IV, Part B. Marek and McCluer,[41] in determining the reaction velocity constant for the thermal dissociation of propane, found that the two principal reactions are dehydrogenation and demethanation; the rates of the two reactions being approximately the same. The data of Frey and Smith[21] also indicated almost an equality between these two reactions for small amounts decomposed at 575° C. With a time of contact of 1 minute they found equal volumes of the propane reacted to form $C_2H_4 + CH_4$ and $C_3H_6 + H_2$.

Butane.—The most careful work on the decomposition of butane was completed by Neuhaus and Marek.[42] Using the same method as Schneider and Frolich, these two workers at Massachusetts Institute of Technology found the primary products of cracking to be :

600° C.	$CH_4 + C_3H_6 = 48{\cdot}5\%$	$C_2H_4 + C_2H_6 = 34{\cdot}5\%$
650° C.	$CH_4 + C_3H_6 = 48\%$	$C_2H_4 + C_2H_6 = 37{\cdot}7\%$ *
600° C.	$H_2 + C_4H_8 = 16\%$	
650° C.	$H_2 + C_4H_8 = 12{\cdot}3\%$	

Hurd and Spence[33] agreed in general with the above data, particularly with regard to the ratio of the products $\frac{CH_4 + C_3H_6}{C_2H_4 + C_2H_6}$, but they found a much smaller percentage of dehydrogenation. Since the reaction times employed by Hurd and Spence were of the order of 20–30 seconds at 600–700° C., a portion of the primary products, butylene and hydrogen, were no doubt lost to the system through secondary reactions.

iso Butane.—Hurd and Spence[33] showed that more than 51 per cent. of the *iso*butane decomposed to form *iso*butylene and hydrogen, whilst

* Approx.

the amount of methane plus propylene formed may have been of the order of 40 per cent. Neuhaus and Marek [43] reported the following amounts of products formed by the cracking of *iso*butane.

600° C. . .	$H_2 + iC_4H_8 = 63\%$	$CH_4 + C_3H_6 = 34{\cdot}5\%$	$C_2H_6 = 2{\cdot}5\%$
650° C. . .	$H_2 + iC_4H_8 = 63\%$	$CH_4 + C_3H_6 = 36\%$	$C_2H_6 = 1{\cdot}5\%$

These data appear to be more accurate than those of Hurd and Spence, and the yields shown may be considered representative for small percentages of decomposition of *iso*butane.

Discussion of Thermal Decomposition of Paraffins.—In considering papers for the foregoing presentation, it became necessary to eliminate much of the work of Pease [47] because of the assumption, which he made, that all the paraffins produced in cracking were methane. He did not make quantitative determinations of the saturated hydrocarbons, which was particularly unfortunate where the percentage decomposition was large. Most of the early data of Hurd and Spence are subject to criticism, since the percentage of decomposition had progressed to such an extent that secondary reactions influenced the formation of the products found. In comparing the data given for the various paraffins, it is interesting to note the decreasing percentage of dehydrogenation of the normal paraffins with increasing molecular size. Dehydrogenation becomes an almost negligible reaction with straight chain molecules which are longer than butane. *iso*Butane and similar branched chain compounds are exceptions, since at least one hydrogen is attached to a tertiary carbon atom. This will be discussed at more length in Section III, Part B.

2. *Olefin Decomposition.*

The data obtained in investigations of the thermal decomposition of paraffins are of necessity more clean-cut than those of the olefins; since the latter not only form fragments of themselves, but to a large extent form polymers as well, which may be quite unstable and decompose spontaneously under the conditions of formation. With the olefins there are two ranges of temperature in which different types of reaction occur, as well as an intermediate range. At low temperatures, and more particularly under increased pressure, the only reactions taking place are those of condensation to polymers of the formula C_nH_{2n}, practically quantitative yields of which have been obtained at temperatures up to some 500° C. In the intermediate range decomposition reactions are just beginning, whilst at higher temperatures, 600–700° C., the products of decomposition are found in appreciable quantities.

Ethylene.—Pease [48] stated that ethane appeared to be a product of the decomposition of ethylene above 525° C. and passed through a maximum at 575–600° C., whilst butylene was the main product below these temperatures. Schneider and Frolich [60] determined the primary products of pyrolysis of ethylene at a temperature of 725° C. and 1/5 atm. pressure. About 70 per cent. of the ethylene reacting formed butadiene and hydrogen. 15 per cent. of the ethylene reacting appears to have formed propylene, whilst a trace of acetylene was always found. How the propylene was formed from ethylene was not suggested by these authors. It appears to

the author, from these data, that butylene was formed by the polymerization of two molecules of ethylene, and at the high temperature of reaction this hydrocarbon instantaneously dissociated to butadiene and hydrogen. The data of Frey and Smith [21] are not of much value in determining the primary products of the pyrolysis of ethylene, because the percentage decomposition was large enough to allow secondary reactions to become appreciable.

Groll [23] made the assumption that propylene rather than butylene was the principal thermal polymerization product of ethylene. An investigation by Lenher [39] and unpublished work by K. R. Edlund were the basis for this assumption, although Lenher in his experiments polymerized ethylene containing various amounts of oxygen and obtained results not unlike those of other investigators [27, 63] using similar active mixtures. A study similar to, but more thorough than, that of Lenher was made by Storch,[62] who found at 377° C. and 141·5 cm. pressure that the addition of 0·02 per cent. oxygen to specially purified ethylene caused the formation of nearly twice the yield of polymers obtained in the absence of oxygen. In addition, butylene appeared to be the primary product of reaction and propylene a secondary product. Unfortunately, the author has no knowledge of the results obtained by Edlund, but it appears at present that the assumption made by Groll [23] is no longer tenable.

Propylene.—The best data published appears to be that of Schneider and Frolich,[60] whose experiments at 725° C. and 1/5 atm. pressure indicated some 50 per cent. of the propylene reacted to form ethylene and butylene, some 30 per cent. to form 5 and 6 carbon olefins with the concurrent production of methane. Other apparently primary products were hydrogen, ethane and butadiene, in smaller amounts. Experiments at one atmosphere and the same temperature were more inconclusive in results.

Hurd and Meinert [31] investigated the pyrolysis of propylene under rather severe conditions where up to 70 per cent. of the propylene disappeared. They found gaseous products in the following general ratio

$$\underset{2}{CH_4} \quad \underset{3}{C_2H_4} \quad \underset{1}{H_2} \quad \underset{1}{C_nH_{2n+2}}$$

where C_nH_{2n+2} was a higher molecular weight than methane. The temperatures of pyrolysis were 600–700° C. An interesting comparison was made by these authors showing the thermal stability of propylene and *iso*butylene to be of the same order.

Butylenes.—Wheeler and Wood,[65] in the pyrogenetic decomposition of α and β butylenes at 600–900° C., found the following reactions to take place:

$$C_4H_8 + H_2 \longrightarrow CH_4 + C_3H_6$$
$$C_4H_8 \longrightarrow 2C_2H_4$$
$$C_4H_8 \longrightarrow C_4H_6 + H_2$$
$$C_4H_6 + \text{Olefin} \longrightarrow \text{Cyclics}$$

The first of these obviously cannot be called a primary reaction, and would only take place after hydrogen had been produced by previous dissociation.

iso*Butylene.*—Hurd and Eilers,[30] using the method of Schneider and Frolich,[60] found two of the primary products of the pyrolysis of *iso*butylene at 700° C. to be methane 39 per cent. by vol. and propylene 32 per cent. by vol. Although their data indicated the primary production of 26 per

cent. by vol. of ethylene, Hurd and Eilers believed it to be a secondary product. To the author this appears to be the best evidence that the data obtained by the zero per cent. decomposition method [60] must be used with discretion; since the formation of ethylene from *iso*butylene requires the rupture of two C–C bonds. The ethylene is probably formed by the decomposition of propylene, one of the primary products, which is less stable at the temperature of reaction than the ethylene. At an earlier date, Hurd and Spence [34] indicated that *iso*butylene between 600° and 700° C. polymerized to the extent of some 50 per cent., whilst the gaseous products of the reaction contained some 50 per cent. methane and 20 per cent. hydrogen. They showed that *iso*butylene decomposed to only 10 per cent. of the extent exhibited by *iso*butane under the same conditions.

B. Theoretical Interpretation of the Decomposition of Hydrocarbons.

Since the empirical decomposition of gaseous hydrocarbons has been discussed and the effective products of the decomposition are known, the visualization of the mechanism by which these products are formed is easier. Only theories of the mechanism have been advanced, as absolute proof has not yet been obtained. The preceding section and the following section may be likened to two branches of chemistry, macro-analytical and micro-analytical. The difference between these two treatments of the thermal decomposition of hydrocarbons is a matter of time, instead of weight as in analytical chemistry. In considering the effective products of primary decomposition, the reaction time is of the order of seconds or even minutes, whilst the half life of free radicals, or possibly the actual primary products, may be about 1×10^{-3} seconds.

Bone and Coward [4] in 1905–1908 postulated the existence of fugitive residues to explain the results they obtained. Williams-Gardner [66] in 1925 also assumed the existence of residues at high temperatures to explain the formation of many products obtained. However, it was a long step from this pioneer work to the experiments of Paneth and co-workers,[44] Taylor and the group at Princeton,[63, 64] Rice and his associates at Johns Hopkins,[56–59] and Bonhoeffer and Harteck.[5] These men worked with metallic alkyls, excited mercury atoms, hydrogen atoms, and even decomposing hydrocarbons. The results of their experiments will be considered briefly in the following section.

Free Radical Theory of Rice.—The papers of Rice [56–59] have been selected as the basis for the discussion of free radicals, because he used a more direct method of obtaining the fundamental units, the values for which are generally agreed upon. His theories are supported in several cases by experimental work which has since been completed, and he has worked with materials under conditions similar to the ones with which this review is concerned. In addition, the calculations made by Rice of the relative strengths of the various bonds are more generally accepted, and his values have been verified partly at least by spectroscopic data. The values which he assigned to the various bonds are shown in Table II, and the strengths are directly proportional to the figures shown.

The experiments of Paneth and Hofeditz [44] and of Rice, Johnston and Evering [59] showed that free radicals, such as CH_3–CH_2–, are produced from metal alkyls and from hydrocarbons. Rice and co-workers have

TABLE II.

C—C = 71·0 kg.-cal.
C=C = 123·8 kg.-cal.
C—H (primary) = 93·3 kg.-cal.
C—H (secondary) = 92·1 kg.-cal.
C—H (tertiary) = 89·3 kg.-cal.

isolated the metal alkyls formed when these free radicals from decomposing hydrocarbons impinged upon a metallic mirror. The gas was passed through a hot (800–1000° C.) quartz zone at 1–2 mm. pressure, and the resulting free radicals struck a metal mirror, of tellurium or another suitable metal, on a cold surface a short distance away. The metal alkyls were collected in a liquid air trap and analysed; butane formed 70 per cent. methyl and 30 per cent. ethyl alkyls, or free radicals, whilst propane produced 80 per cent. methyl and 20 per cent. ethyl alkyls. The investigators calculated the half life of these radicals to be about 1 or 2×10^{-3} seconds. Possibly because of the nature of the apparatus, they could obtain no traces of free radicals at 70 mm. pressure.

Rice in 1931 [56] postulated the decomposition of ethane by a chain mechanism, although later,[58] as the result of further work, he found "either the formation of ethylene and hydrogen from ethane goes through a free radical mechanism, or the free radical mechanism and a simple separation of hydrogen occur simultaneously." Since Rice did not find any free radical formation in the range 550–650° C.,[59] and did find free radicals formed from ethane at 890–950° C.,[58] it seems most plausible to the author that simple elimination of a molecule of hydrogen from a molecule of ethane takes place almost exclusively at the lower temperature; whilst free radical formation increases more rapidly with temperature and predominates at the higher temperature. Calculations made by Pichler [52] tend to support this theory.

Since Rice first published his theory, several experimental verifications have been made, and the agreement has been good in most cases, particularly with C_4 to C_6 hydrocarbons. The amount of H_2 formed experimentally does not check the calculated theoretical as well as does the formation of other products. Neuhaus and Marek [42] obtained very good agreement with the predictions of Rice in the decomposition of butane. Using the nomenclature of Rice,[56] the following equations depict the decomposition of butane.

P_1 $CH_3\,CH_2\,CH_2\,CH_3 \longrightarrow CH_3^- + CH_3\,CH_2CH_2^- - 71$ kg.-cal.

P_2 $CH_3\,CH_2\,CH_2\,CH_3 \longrightarrow 2CH_3\,CH_2^- - 71$ kg.-cal.

S_1 $CH_3\,CH_2\,CH_2^- \longrightarrow CH_2 = CH_2 + CH_3^- - 18{\cdot}2$ kg.-cal.

S_2, S_3 Same as A_1 and A_2 where $R = CH_3\,CH_2\,CH_2^-$

A_1 $CH_3\,CH_2\,CH_2CH_3 + R^- \longrightarrow RH + CH_3CH_2CH_2CH_2^- \longrightarrow$
$RH + CH_2 = CH_2 + CH_3 - CH_2 \longrightarrow CH_3CH_2^-$
$\searrow CH_2 = CH_2 + H$

A_2 $CH_3CH_2CH_2CH_3 + R \longrightarrow RH + CH_3\,CH\,(CH_2CH_3)^- \longrightarrow$
$RH + CH_3CH = CH_2 + CH_3^-$

(P indicates a primary reaction, S a secondary reaction and A is a chain reaction.)

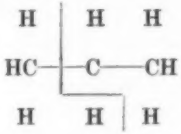
In these chains the carrier radicals are CH_3^-, CH_3 CH_2^- and H atoms. The work of Neuhaus and Marek [42] on *iso*butane did not agree as well with the predictions of Rice. However, recently published work by Frey and Hepp [19] showed quite good agreement, particularly with *n*-pentane and *n*-hexane. For a more exhaustive study of free radical formation, the reader is referred to the original articles.[56–59]

The free radical theory of Rice is valuable to the modern research worker because it offers a convincing explanation of some data which were otherwise meaningless. Schneider and Frolich [60] found ethane and butane were formed in the primary decomposition of propane. Such products could be formed from free radicals as shown below.

$$CH_3CH_2^- + CH_2CH_2^- \longrightarrow C_4H_{10}$$
$$CH_3^- + CH_3^- \longrightarrow C_2H_6$$
$$\text{and } CH_3CH_2CH_2^- + CH_3^- \longrightarrow C_4H_{10}$$

Rice has calculated from data in the literature the relative strengths of the primary, secondary and tertiary C–H bonds to be 93·3, 92·1 and 89·3, respectively. These values may explain the larger production of hydrogen found in the decomposition of *iso*butane compared with normal butane decomposed under the same conditions. A plausible explanation of the formation of butadiene from ethylene at about 700° C. is obtained from energy considerations. Two molecules of ethylene collide, but the energy, that would be made available by their combination to butylene, is some 21 kg.-cal., or nearly the amount necessary for the activation of the reaction $C_4H_8 \longrightarrow C_4H_6 + H_2$. In this case, instead of the two molecules flying apart again, if a third body were not present to retain part of the available energy, the butylene might conceivably lose a molecule of hydrogen. This is an assumption similar to that made by Pichler.[52]

The investigations of Kassel [38] and of Burk [7] do not agree with the theories of Rice. They believed the molecule may split thus—



and that the group $=CH\ CH_3$ was responsible for the effects obtained by Rice. This seems scarcely possible in view of the isolation of metal alkyls which have been formed from free radicals. Bonhoeffer and Harteck [5] showed that ethylene, ethane and hydrocarbons other than methane could be attacked by hydrogen atoms and stripped to less hydrogenated compounds. Taylor and Hill [63] published results of their work on the reactions of ethylene and hydrogen in the presence of excited mercury atoms. They followed reactions at lower temperatures than those with which this paper is concerned, the results of which indicated the formation of free radicals. Taylor and Jones [64] decomposed metal alkyls and, by means of the active radicals formed, obtained yields of the order of 20 per cent. of polymers from ethylene under conditions where no polymers were formed from ethylene alone. The liquid was, however, not formed by the radicals themselves. This introduces the concept that polymeriza-

tion requires only activation of the molecules for the reaction to proceed. This activation need not necessarily be supplied in the form of heat energy.

In connection with the theory of hydrocarbon decomposition, Pease [47] has offered a qualitative statement explaining the relatively greater instability of the higher molecular weight molecules. "Modern theories of reaction rate indicate that a molecule which is about to react contains energy in excess of the average of all molecules. More particularly, the excess is associated with one or more degrees of freedom, which, in the cases under consideration (ethane, propane and the butanes), doubtless represent the oscillation of atoms about their positions of equilibrium. Heat capacity data prove that the total energy available for concentration on some particular degree of freedom increases with the number of atoms in the molecule (and also, of course, with the temperature). The frequency with which a molecule finds itself active will therefore be greater the more complex the molecule, so that if the energy required for activation is of the same order for molecules of two substances of differing complexity, the frequency with which the more complex molecules react will be the greater." This theory is substantiated in part by the calculations of Paul and Marek [46] from original and published data showing greater ease of dissociation of the normal paraffins of increasing molecular weight.

IV. YIELD OF LIQUID PRODUCTS OBTAINED BY THERMAL TREATMENT OF HYDROCARBON GASES.

In perusing the literature, it becomes apparent that many investigators, even to quite recent years, have not considered time of reaction as an important variable. This is evident not only from the way the apparatus was constructed, but also from the way the calculations were made. Temperature was considered the main variable, and since superatmospheric pressure investigations were difficult at high temperatures, there are very few publications of work at elevated pressures.

Discussion of Some Variables.—The first clear statement of necessity for considering the time of contact was enunciated by Fischer [17] and co-workers. "With rising temperature the appearance of free carbon increases rapidly. This undesirable decomposition can be prevented by a suitable decrease in the time of contact." While this statement was made primarily concerning the pyrolysis of methane, it is considered applicable to the group of compounds under consideration, C_2 to C_4 hydrocarbons. Hurd and Pilgrim reported [32] that as a result of experiments with butanes similar results may be expected in reaction tubes of varying sizes if a constant contact time is maintained, whilst Frey and Hepp, in a recent paper,[18] obviously gave careful consideration to the time of reaction, they clearly outlined the useful results which may be obtained by control of the time element in obtaining an optimum yield of volatile liquid (essentially motor stock). These yields were all of the same order, some 12 to 14 per cent. for a gas containing 18·6 per cent. methane, 44·7 per cent. propane, 32·7 per cent. butane and 4·0 per cent. *iso*butane, between the temperatures of 700° and 1050° C. The interdependence of volatile oil, tar and coke yields is illustrated by Fig. 1, taken from their data. The

optimum time of contact for this mixture varied from 0·03 second at 1050° C. to about 4 minutes at 700° C. The figures given are for atmospheric pressure. A novel means of controlling the time element in an industrial polymerization process was disclosed in a recent patent [1] whereby the most refractory portion of the mixed hydrocarbon gas is subjected to the highest temperature and the longest reaction time, whilst the portion most easily decomposed is treated at a lower temperature and for a shorter period of time. The character of the product obtained can be controlled.

Recent work by Cambron and Bayley [10] has shown the desirability of turbulent flow in reactor tubes rather than stream-line flow. It appears

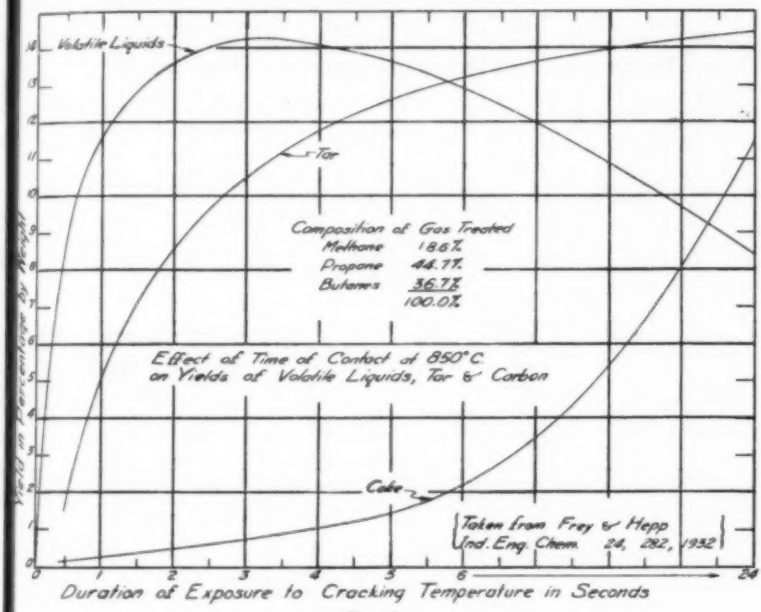


FIG. 1.

that turbulent flow, as induced by baffles, causes the production not only of larger quantities of liquids in the pyrolysis of gaseous hydrocarbons, but of higher yields of olefins as well. These principles may well find application on an industrial scale when more is known about them. It is of interest that Cambron and Bayley obtained an optimum yield of 23·3 lb., or about 19 per cent. by weight, of light oil or naphtha based on the propane processed at 930° C. The total percentage by weight of liquids produced was about 27·4, or somewhat more than that obtained by other investigators. Slightly higher yields were obtained in quartz tubes.

Since many early investigators were primarily concerned with the gaseous products, no particular effort was made for isolation of the liquid products. The isolation of the liquid products is a problem in itself, since it requires some type of fog precipitation apparatus or an additional

condensing and preferably scrubbing operation at either a low temperature or a high pressure. Zanetti [67] was the first to realize the value of using electrostatic precipitation in the collection of the tar and heavier products formed by pyrolysis. Because many investigators did not make a material balance on their system, and because many were not cognizant of the facts outlined above, the yields of liquid polymers as reported in the literature, almost without exception, tend to be low rather than high. They may, therefore, be considered minimum rather than maximum yields.

Since it is necessary to treat gaseous paraffins at rather elevated temperatures to obtain olefins therefrom, and since at such temperatures a rather heterogeneous decomposition takes place, it is not surprising that

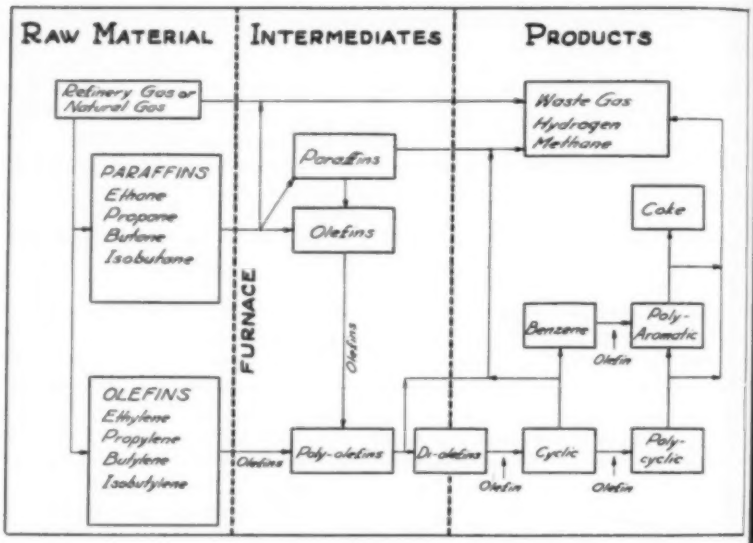


FIG. 2.

PYROLYSIS OF REFINERY GASES.

many experiments to accomplish the dehydrogenation catalytically at lower temperatures have been made. Untold numbers of catalysts have been tried in various forms, and none of them appears at present to have a chance of commercial success. It is only recently that Frey and Huppke [39] have succeeded in determining equilibrium constants of the system:

$$\text{Olefin} + \text{Hydrogen} \longrightarrow \text{Paraffin}$$

with a specially prepared catalyst of chromic oxide gel. Even at these low temperatures in the neighbourhood of 400° C. the life of the catalyst was short—some 4 hours. Almost without exception the catalytic materials seemed to hasten the reaction paraffin $\longrightarrow$ carbon + hydrogen, perhaps not directly, but carbon and hydrogen were the end products obtained. Intermediate products except methane have not been isolated. The catalysis

of the two reactions, dehydrogenation of the paraffins and polymerization of the resulting olefins by the use of a single catalytic agent, at the present time presents a dour outlook.

It may be enlightening at this time to consider the process of polymerization from the standpoint of raw materials, intermediates and products. This has been outlined in Fig. 2. The reactions shown on this chart were discussed in Section II, and the chart is shown to indicate the relation between the previous discussion and the commercial utilization of natural gas or refinery gas.

Summary of Some Yields Reported.—The most illuminating contributions to the literature in this field are those on the thermal decomposition of paraffins made by Hague and Wheeler,[25] on the pyrolysis of olefins by Wheeler and Wood,[65] and on the decomposition of both types made by Frey and Hepp.[18, 19] The data published by these authors and that by Groll [23] have been in some cases recalculated, and are shown in Table III.

TABLE III.

Once Through Yields.

Hydrocarbon.	Temp. (° C.).	Reaction time in secs.	Wt. % of mot. stk. end-point 170° C.	Wt. % total liquids.	Weight %.		
					CH_4.	H_2.	Coke.
		Hague and Wheeler.[21, 22]		Wheeler and Wood.[65]			
Ethane	850	10–20	11·2	17·9	28·9	4·6	—
Propane	850	,,	11·6	23·1	33·9	2·4	0·9
Butane	800	,,	12·9	20·4	30·3	1·9	—
Ethylene	800	,,	17·7	36·1	19·3	1·2	1·4
Propylene	750	,,	20·4	35·6	18·1	0·7	trace
Butylene	700	,,	23·6	35·8	17·2	0·4	,,
β-Butylene	700	,,	25·8	37·0	17·4	0·4	,,
		Frey and Hepp.[14, 15]					
Butane	850	7·2	17·0	34·0	(not calculated)		
Ethane	850	3	10·5	13·5	,,		
Propane	850	2·4	15·5	23·5	,,		
Ethylene	725	60	23·5	42·0	,,		
		Groll.[23]					
Propylene	800	9*	about 20	40·0	—	—	—
Propane	800	7*	,, 7	13·2	—	—	—
Butane	775	7*	,, 8	16·0	—	—	—
β-Butylene	800	7*	,, 20	40·0	—	—	—

* Estimated from data; may be only half the time shown.

No attempt has been made in correlating these data to calculate material balances, as in most cases the data given in the original papers were insufficient to do so. The yields which are shown in Table III are among the highest that have been reported to date. The temperatures reported in Table III, and most articles in the literature, may not be true gas temperatures, but they indicate the temperature range. Although the temperatures shown are higher than those which may be used at present for profitable commercial operation, the data indicate the relative amounts of naphtha and tar that can be produced from the various pure gaseous hydrocarbons.

The most outstanding feature of the results obtained by Wheeler and co-workers was the division of pyrolysis into two ranges divided by a temperature of some 750° C. In treating the paraffins below that temperature, ethylene built up in the system, and coke, if found at all, existed only as traces. In the lower range each hydrocarbon reacted individually, but in the upper range the reaction products were quite similar for all of them. This was, of course, true only for a given time of contact—in these experiments some 10 to 20 seconds. The data in Table III indicate that the maximum yields which can be obtained from olefins are in general some 100 per cent. greater than from paraffins, with a correspondingly smaller yield of methane and hydrogen or waste gases. The maximum yield of liquids is obtained from the olefins at a temperature some 100° C. lower than from the corresponding paraffins. The indications, not only in these data, but throughout the literature, are that a certain olefin concentration at a given temperature and time of reaction is necessary for a definite yield of liquid. This conclusion is corroborated by calculations from unpublished data obtained in these laboratories, showing the partial pressure of olefins present during the pyrolysis of hydrocarbon gases under super atmospheric pressure, to be of the order of five atmospheres in some cases. As would be expected, appreciable yields of liquids are obtained under these conditions at lower temperatures or with shorter times of contact than recorded in the literature. Piotrowski and Winkler [53] arrived at a similar conclusion by working with gases containing methane and varying amounts of hydrocarbons heavier than methane. They found that for each of these gases there was an optimum time and temperature, the time being inversely proportional to the content of hydrocarbons heavier than methane, or it was shortest at a given temperature for a gas containing no methane.

In the data of Wheeler and co-workers, it is interesting to note that the maximum yields were obtained for both ethylene and ethane at a temperature some 50° C. higher than for the C_3 or C_4 corresponding hydrocarbons. This is particularly noticeable with the paraffins, where the speed of cracking seems to be more directly influenced by the temperature. The liquid product obtained by them consisted mostly of *cyclo*hexene, *cyclo*hexadiene with some benzene, and their methyl derivatives at the lower temperatures. At the higher temperatures, the proportional amount of tar increased considerably, and the lower-boiling material was substantially benzene and toluene. The best yields of naphtha in appreciable amount were some 60–70 per cent. of the total, at a temperature lower than that necessary for the maximum yield of total liquids. Some interesting comparisons were made in these papers of experiments carried out with horizontal and vertical silica tubes. In each case the amount of total liquid obtained in the horizontal tube was some 80 per cent. of that obtained in the vertical tube. Part of the remainder appeared as coke. Frey and Hepp [18] found some coke to consist of microscopic globules, apparently formed in the gas phase and subsequently deposited. This leads to one of two conclusions: either the reactants in the tube are not homogeneous, consisting in part of minute droplets, or the heavier materials which may contact with the surface in the horizontal tube do not have an opportunity to be removed from the reaction zone by gravity. In

any case, the yield of liquid material is substantially lowered, and the yields of methane and hydrogen are increased, in horizontal tubes.

The data of Frey and Hepp [18] are in some respects of more value than the data of Wheeler and co-workers, particularly in that more complete analyses were given. Frey and Hepp do not cover the raw material field as completely, but where reported their work agreed quite well with that of Wheeler and co-workers. In fact, Frey and Hepp obtained in one case a substantially higher total liquid yield from butane at 850° than did Hague and Wheeler. This yield was 17 per cent. volatile oil and 17 per cent. tar. The yields from ethane, ethylene and propane were of the same order as obtained by Wheeler and co-workers. Groll [23] stated that "propylene is outstanding in the formation of aromatics by pyrolysis. No other hydrocarbon of low molecular weight gives higher yields. Only the high boiling oils give slightly higher yields." Yet in the same table where there was shown a liquid yield of 40 per cent. by wt. from propylene, a liquid yield of 40 per cent. by wt. was also shown for butylene. It appears to the author that Groll has attempted to simplify drastically the effect of a large number of reactions taking place during the pyrolysis of a hydrocarbon, but in so doing has made some assumptions which are not fundamentally sound, thereby weakening his case. Hague and Wheeler [28] have made somewhat similar comments on this same paper by Groll.[23]

Piotrowski and Winkler [53] pyrolyzed a gas containing propane 39 per cent., butane 50 per cent., and pentane 11 per cent. From this gas, at 870° C. and about 8 seconds reaction time in a chrome-nickel steel tube, they obtained 13 per cent. motor stock, 8 per cent. tar and some 7 per cent. coke. At 730° C. they obtained only some 3 to 4 per cent. motor stock and some 6 per cent. of soot. To these investigators the indications were that the carbon once deposited is a catalyst for more carbon deposition. The author does not believe this statement should be taken generally; it is probably due to their particular conditions of experimentation. Zanetti [67] obtained yields of the order of 15 per cent. of tar in an electrostatic precipitator after passing through it the propane–butane fraction of natural gas, which had been decomposed in a quartz tube. No attempt was made to retain vaporized liquid which makes his liquid yields appear low.

Davidson,[12] who did some very good work at an early date, only indicated the yields of liquid products obtained from the ethane–propane fraction of natural gas condensate. He is one of the few who conducted experiments at elevated pressure. Whilst he did not indicate the yields obtained by passing the gas through a copper tube, he believed aromatic formation was repressed by pressure above 700° C. This is not necessarily the case, as he measured aromatic formation by tar fog. As an increase of pressure decreased the evolution of hydrogen and increased the evolution of saturates such as methane, it may have repressed the formation of aromatics from the hydrogenated cyclics first formed. The hydrogenated cyclics might form a lighter-coloured fog, which may have led Davidson to this conclusion. In addition, Davidson did not maintain time of contact constant while increasing the pressure, which fact detracts from the value of his results.

The work of Podbielniak [54] is illuminating when considered analytically.

He believed the best yields could be obtained at very short times of contact, with consequent small yields of methane and hydrogen. Therefore, his work was mainly limited to a consideration of temperature as a variable. Podbielniak worked with a semi-commercial plant having a capacity of 25,000 cu. ft./day through alloy metal tubes with a reaction temperature at the outlet of the radiant tubes of 1500–1750° F. (about 820–950° C.). The charge to the unit was a natural gas condensate, and at 1740° F., 2·7 gallons of liquid, or 16 per cent. by wt. were obtained per 1000 cu. ft. of gas processed. This result was the maximum yield obtained, typical data for which follow :

Charge Vol.-%.

H_2.	CH_4.	C_2H_6.	C_3H_8.	C_4H_{10}.	C_5^+.
0·0	2·1	10·0	76·2	11·5	0·2

Residual or Cracked Gas Vol.-%.

H_2.	C_1.	C_2.	C_3.	C_4.	C_5^+.
0·6	78·7	14·8	1·3	1·0	3·6

The volumetric ratio of cracked to raw gas was 2·11. Most of the liquid yield was the 3·6 per cent. of C_5, and heavier in the cracked gas which was obtained by compression to 300 lb. with subsequent scrubbing at that pressure.

In considering these results, there was produced 1639 cu. ft. of methane per 1000 cu. ft. of charge, or a yield on a once-through basis of 60 per cent. by wt. of methane, while there was formed some 16 per cent. by wt. of synthetic crude. Frey and Hepp, and also Hague and Wheeler, produced from propane, which was substantially the gas Podbielniak used, at somewhat lower temperatures some 25 per cent. by wt. of liquid hydrocarbons with 40 to 50 per cent. by wt. of methane and hydrogen. Although Cadman [8] obtained much smaller yields on a semi-commercial scale than did Podbielniak, it would seem that the point made by the latter—namely, that short contact time is desirable—is a doubtful one, particularly as it involves operation at a higher temperature than appears necessary. A peculiar figure in Podbielniak's data is the almost negligible amount of H_2 formed. The H_2 perhaps has contributed to the formation of CH_4 under these conditions. This is particularly unfortunate from the standpoint of ultimate yield if a re-cycling process were contemplated. In making a comparison of the yields of Podbielniak with those of Frey and Hepp,[18] the latter obtained nearly equal volumes of H_2 and CH_4 from the propane at 1050° C. with a contact time of 0·03 second. It is possible, of course, that this result was caused by the difference in surfaces, as Frey and Hepp used a silica reaction tube in which they obtained a higher yield, some 26 per cent. total liquids. It is interesting to note that the coke formed in the tubes used by Podbielniak required air blowing for 15 minutes every 8 to 12 hours of operation, although he believed that the life of such tubes in a commercial installation should run into many thousands of hours at the cracking temperature required for maximum aromatics.

Dunstan, Hague and Wheeler [13] presented some interesting general figures on the pyrolysis of paraffins under pressures up to 150 lb./sq. in.

in the temperature range 725–800° C. The maximum yield obtained was 12·4 per cent. by wt. of the ethane passed at 750° C. and 150 lb. compared to a maximum of 22 per cent. at atmospheric pressure and a higher temperature. Similarly, the influence of pressure up to 150 lb./sq. in. was studied on the polymerization of ethylene at 600–700° C. The largest amount of liquid obtained was 35 per cent. by wt., and by a suitable adjustment of the temperature and time of contact, this figure was approached at several pressures. The production of 36·1 per cent. by wt. at atmospheric pressure was not improved upon, but the working temperature was reduced over 100° C. by the application of pressure; a similar conclusion was arrived at by Cambron and Bayley.[10] Dunstan, Hague and Wheeler found that increasing pressure appeared to accelerate the deposition of carbon, although it was not disclosed whether or not the deposition of carbon was accelerated more than the formation of liquids.

Conclusions on Yields Obtained.—In general, the results of work which has been published show the following: Yields up to some 25 per cent. by wt. of liquids have been obtained by pyrolysis of the paraffins at atmospheric pressure, whilst up to some 40 per cent. by wt. have been obtained from the olefins under similar conditions. These data, if applied to a gas composed of 50 per cent. olefins and 50 per cent. paraffins, would give results under the conditions of experimentation [25 and 65] as follows:

Ethane–Ethylene 800° C.

Motor Stock End-point 170° C.	= 12 wt.-%
Total Liquids	= 23 „ „
Vent or Inert Gases	= 21 „ „

Propane–Propylene 750° C.

Motor Stock End-point 170° C.	= 12 wt.-%
Total Liquids	= 21 „ „
Vent or Inert Gases	= 19 „ „

From which the conclusion is reached that, processing such gases with recycling, an ultimate liquid yield of the order of 50 per cent. would be expected in this range where coking is not appreciable, whilst the motor stock would be some 60 per cent. of the total liquid produced. Or from refinery gas, a lower ultimate yield of motor stock would be obtained, because the ratio of paraffins to olefins is greater than one.

The best published work on thermal polymerization under pressure is by Frey and Hepp.[18] In this work they have not bettered the yield obtained under atmospheric pressure, and while no direct comparison can be made, the percentage of methane formed appeared to be higher than at atmospheric pressure.

Other work on pressure, at temperatures above 500° C., which has been published, tends to show that the yields at atmospheric pressure have not been bettered, principally perhaps because of excess formation of methane under pressure. This conclusion is not borne out by unpublished data obtained in these laboratories. No increase was observed in the amount of methane formed, and at shorter times of contact under pressure there

appears to be a higher ratio of motor stock to tar which tends to increase the ultimate yield of motor stock.

From a survey of the literature it appears that certain things are unavoidable, and the thermal decomposition of hydrocarbons in every conceivable manner is one of them. Therefore, in attempting to control this decomposition, it would appear that Frolich and Wiezevich [22] were theoretically correct in stating that a two-stage process would give better yields—for example, 10 gallons of product/1000 cu. ft. of propane charged or a 65 per cent. yield by weight of the original propane. This type of process is one in which the cracking takes place at atmospheric pressure and a high temperature, thus obtaining large quantities of olefins in this first stage. The reactants are partially cooled, and the hydrogen is removed by selective oxidation over a catalyst such as CuO, or the reactants may be cooled to such a temperature that the hydrogen could be removed by fractionation. The second step consists in polymerizing the olefins in the gas at a high pressure and a sufficiently high temperature to yield the type of product desired. This step may be accomplished with practically no loss to methane and hydrogen. The I.G. Farbenindustrie [35, 36] used two reactions to accomplish this second step in the production of aromatics. First, the olefins were polymerized nearly quantitatively under 40 atmospheres pressure and a rather low temperature, 400° C., in the presence of suitable catalysts such as activated charcoal. The liquids thus obtained are converted in the second step to aromatics by subjecting them to a dehydrogenating catalyst such as ammonium molybdate at 600° C. Whilst this process appears attractive theoretically, it becomes obvious that as the number of steps increase, the economic desirability of the process dwindles because of the heating and cooling involved between steps. An industrial process must produce not only attractive yields, but also be economically profitable, and this last requires simplicity of operation.

V. MISCELLANEOUS FACTORS AFFECTING THE PYROLYSIS OF HYDROCARBON GASES AND THE FORMATION OF LIQUIDS THEREFROM.

There are numerous miscellaneous factors affecting the yield of liquid hydrocarbons obtained by pyrolysis of the gaseous paraffins and olefins. Such factors are the dilution of reacting hydrocarbon gases, and the surface in contact with the gases.

A. Diluents.

1. *The Effect of Hydrogen.*—The reported effects of hydrogen on the reaction vary considerably, although most investigators who have considered this phase of the problem agree that hydrogen does affect the reactions. No exact study of the subject has been made. The data of Frey and Smith [21] indicate the effect of hydrogen on the pyrolysis of propylene plus hydrogen, and ethylene plus hydrogen. The experiments were made at 575° C. and atmospheric pressure with a time of contact of 4 minutes.

	C_2H_4.	$C_2H_4 + H_2$.	C_3H_6.	$C_3H_6 + H_2$.
Charge	100%.	48·9 + 49·9	100%	43·7 + 54·7
Products, vol.-%.				
N_2	0·8	0·9	0·4	0·7
H_2	0·8	42·8	1·7	48·4
CH_4	2·6	2·2	10·7	7·5
C_2H_4	84·4	39·3	8·0	5·2
C_2H_6	3·2	13·1	1·9	1·7
C_3H_6	4·5	} 1·7	68·9	31·3
C_3H_8	0·0		3·0	3·0
Heavier	3·7		5·4	2·4

Considering these results, more ethylene appears to have reacted in the presence of hydrogen than in the case of pure ethylene, but the ethylene reacting has nearly all been hydrogenated. Hydrogen has been removed from the system as such. The decreased formation of heavier material is greater by far than that caused by the diluent effect of hydrogen alone. In the presence of propylene, as with ethylene, about the same amount of hydrogen disappeared, but in this case it appears to have increased the percentage of methane, and to a smaller extent of ethane and propane. The amount of heavier material formed has not been decreased, but attention is called here to the discussion in Section V, where it was shown that the ultimate yield of liquid from paraffins was much lower than from olefins because of the higher production of waste gases. Therefore by hydrogenating olefins the ultimate liquid yield is decreased by a larger amount than that obviously shown in the above data.

Pease [48] has made some instructive investigations with ethylene mixed with nitrogen and hydrogen. Nitrogen is a satisfactory diluent, and he should, therefore, have found any effect of hydrogen other than the merely diluent action.

Reaction tube volume 637 ml., total gas flow rate 40 ml./min.

Temp. (° C.).	Reacted, ml.		Formed, ml.		
	C_2H_4.	H_2.	C_2H_4.	CH_4.	C_nH_{2n}.
	50 ml. Ethylene–50 ml. Nitrogen.				
550	5	—	2	0	2
575	8	—	3	0	2
600	11	—	5	2	4
	50 ml. Ethylene–50 ml. Hydrogen.				
550	10	9	7	0	2
575	14	11	11	0	2
600	21	16	14	4	1

An inspection of these results makes it quite clear that hydrogenation does not take place independent of condensation. Twice as much ethylene reacted in the presence of hydrogen as in the presence of nitrogen, although nearly all of the excess reacting formed ethane. From this and other data reported, Pease came to the conclusion that the hydrogen activated the ethylene for subsequent reaction with itself (hydrogen).

Hurd and Meinert [31] have obtained similar results with propylene. The

amount of methane or ethane formed in an H_2–C_3H_6 mixture was greater than in an N_2–C_3H_6 mixture, and the amount of propylene reacting was greater. A large quantity of hydrogen was removed from the mixture as such by reactions which had occurred. They believe this indicated hydrogenation of the CH_3^- residues which may be formed momentarily by splitting of the C–C bond. A different view of this phenomenon was advanced by Frey and Hepp,[18] who stated that the hydrogenation of olefins higher than ethylene took place in the presence of hydrogen, with the subsequent formation of methane caused by cracking these paraffins. In this way the large amounts of methane at long contact times are produced. These investigators also showed that with a 50 per cent. mixture of H_2 and C_3H_8 at 850° C. and a contact time of three seconds, the total liquid yield was lowered from 23·5 per cent. to 15·5 per cent. by the addition of the hydrogen. Dunstan, Hague and Wheeler [13] stated that the yield of aromatic hydrocarbons from methane was reduced 50 per cent. by a hydrogen concentration of 15 per cent., whereas such reduction was not noted in the case of nitrogen. Bradley and Paar [6] have shown that hydrogen promoted the decomposition of toluene and xylene to methane and benzene.

It would appear, therefore, that while the action of hydrogen is not definitely known regarding its effect on the decomposition reactions of the paraffins, it does have a marked effect on the subsequent polymerization of the olefins in reducing the yield of liquid and increasing the yield of waste gas, thus decreasing the ultimate yield of liquid polymers. Any process which contemplates the pyrolysis of hydrocarbon gases to form liquids in the presence of appreciable amounts of hydrogen is inefficient.

2. *Water Vapour.*—Propane containing some 30 per cent. of water vapour has been pyrolyzed by Boeckeler.[3] No catalytic effect of the water vapour was observed, nor was there any evidence of carbon monoxide or dioxide in the off gas to indicate the presence of the water gas reaction. The water vapour seemed to act merely as an inert diluent even to a temperature of 1050° C. A contrary opinion was expressed by Groll,[23] who found that steam inhibited the formation of coke when cracking hydrocarbons in iron tubes. Unfortunately, Groll in carrying out his experiments did not maintain other variables constant, particularly time of contact, which leaves his results somewhat open to question. It appears to the author, from the data of Groll, that he succeeded in deactivating the iron with the steam, and that, as concerns the pyrolysis, the water vapour had no effect.

3. *Oxygen.*—Several references have been made in the literature to the peculiar effect of oxygen on the pyrolysis of hydrocarbons under normal pressure. The effect seemed to be unusual in that small amounts of it improved the production of liquid, whilst larger amounts acted merely as a diluent.[13] Under other conditions [63] small quantities of oxygen added to a system containing hydrogen and ethylene caused a very large increase in rate of reaction of the ethylene until the oxygen was used up. As previously mentioned,[62] the presence of added oxygen exerted an unusual effect on the polymerization of specially deoxygenated ethylene, 1 molecule of oxygen appeared to cause about 85 additional molecules of ethylene to polymerize. This phase of gaseous polymerization is one which has been neglected, but will no doubt be further investigated because of the interesting industrial possibilities.

B. Effect of Various Surfaces.

Reference has been made to the homogeneous decomposition of hydrocarbons. Some of the surfaces found to be inactive and the investigators follow :

Surface.	Hydrocarbon.	Investigator.
Glass (Pyrex) . . .	C_2H_6	Hurd and Meinert.[31]
Glass	C_2H_6, n-C_4H_{10}, and i-C_4H_{10}	Pease and Durgan.[50]
Silica	C_2H_6, C_2H_4, and H_2	Frey and Smith.[21]
Copper	C_2H_6	,, ,,
Chromium Steel (ascoloy) .	C_2H_4, C_2H_6, and i-C_4H_8	Hurd and Eilers.[30]

In general, investigators [11, 6] have found silica to be an inactive surface or nearly so with copper following it closely. Copper may be slightly catalytic.[11, 3] Surfaces such as iron, nickel and monel metal promote decomposition to carbon and hydrogen. The I.G. Farbenindustrie [35, 36] specified using copper, silver, gold and alloys of these noble metals or ferrosilicon; also tinned, galvanized, aluminium or chromium plated iron or copper as the lining for reaction vessels, and as catalysts in the pyrolysis of hydrocarbons. Dunstan, Hague and Wheeler,[14] in polymerizing ethylene, found that stainless steel and aluminium liners gave results similar to copper, with rather more deposition of carbon. One of Hadfields Steels, Era 131, showed a marked advantage over copper as a liner in the polymerization of ethylene at temperatures up to some 500° C. Another steel appearing to be good was Hadfields H.R. 2. In a rather comprehensive investigation, Hurd and Eilers [30] indicated the inactivity of surfaces in which olefins are pyrolyzed; quartz, glass and chromium steel (Ascoloy) being non-catalytic, whilst nickel, iron and monel metal became progressively better catalysts for carbonization and dehydrogenation. Poisoned surfaces such as those treated with KCl, clay surfaces and similar surface materials have been found to be inactive. There appears to be a rather wide range of surfaces suitable for the pyrolysis of hydrocarbons to aromatic or hydroaromatic liquids.

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THE SPECIFIC REFRACTION AND OTHER PHYSICAL CONSTANTS IN CONNECTION WITH THE DESTRUCTION OF MINERAL OILS.*

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INTRODUCTION.

THE main purpose of the investigation was to study changes in the cyclic character of an oil at a high temperature (435° C.), under high hydrogen pressure (initial pressure 100 kg./cm.^{2}), without a catalyst and in the presence of hydrogenation catalysts such as nickel and molybdenum. It was of interest to compare the behaviour of an oil rich in aromatic compounds and an oil rich in naphthenes, containing a small amount of aromatic compounds. Therefore a Borneo lubricating oil fraction was separated into an extract and a refined product, by selective extraction using liquid sulphur dioxide diluted with some benzene as an extraction-solvent. As raw materials for the experiments the extract and the refined product were used.

In a previous communication the extraction and the properties of the products obtained have been described.[1]

THE EXPERIMENTS.

The refined product and the extract were submitted to three experiments. About 400 g. of oil were heated in a rotating Bergius autoclave of Siemens-Martin steel at 435° C. during 1 hr. under high hydrogen pressure (initial pressure at room temperature about 100 kg./cm.^{2}).

In the first experiment (A) no catalyst was used (berginization), in the second experiment (B) molybdenum was used as a catalyst (40 g. of molybdenum-on-carbon), and in the third experiment (C) 40 g. of a nickel catalyst (nickel on kieselguhr) was used.

After cooling the autoclave, the quantity and the composition of the gases formed during the experiment were determined.[2]

From these values it was possible to deduce the magnitude of the change to very low-boiling compounds. However, under these conditions, the extract and the refined product proved to be very resistant, as far as the formation of gases and very low-boiling compounds is considered (less than 5 per cent. of these products were formed). The reaction products had a lighter colour than the very dark raw material; the product of the experiment without a catalyst had become red-brown, while the reaction products from the catalytic hydrogenations were lighter still, especially with molybdenum as a catalyst (brown-yellow).

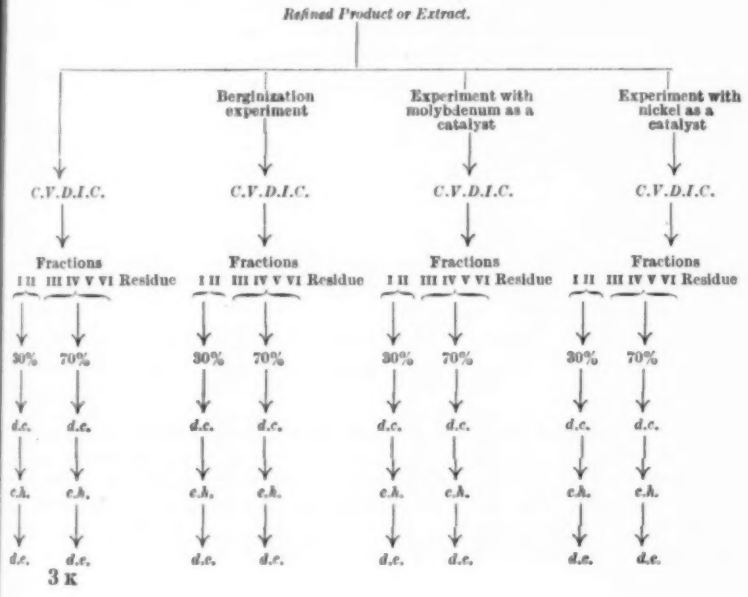
The liquid reaction products obtained were distilled in vacuum, followed by cathodic-light vacuum with internal condensation.[3]

* Paper received March 12th, 1935.

Six fractions were taken, each fraction having a volume of about the $\frac{1}{10}$th part of the charge to the distillation vessel.

The intention was to investigate the nature of the different parts of the reaction product, and especially to ascertain if their character was the same. No important difference was observed, and therefore a more detailed investigation was carried out by combining some of the fractions so that the reaction product, divided into two parts, was analysed completely. The last four fractions (the high molecular fractions) were combined after having determined the physical constants. The last-mentioned products represent about 70 per cent. by weight of the total reaction product, and will be indicated in the following by "70 per cent. fraction." The first two fractions also were combined: "30 per cent. fraction." These 30 per cent. and 70 per cent. fractions of the refined product, of the extract and also of the reaction products obtained were analysed, then completely hydrogenated at relatively low temperatures ($< 310°$ C.) and again analysed after hydrogenation. The composition of the hydrogenated products and also of the products before hydrogenation could be calculated by the method of Vlugter, Waterman and v. Westen.[4]

The materials used will be indicated by G, the raw material; A, the products from the berginization experiment; B, the experiment with molybdenum catalyst; C, the experiment with nickel catalyst. The raw material from which the reaction product is obtained will be denoted by R, refined product, and E, extract. Thus, AE70 represents the 70 per cent. fraction of the berginization experiment on the extract. The course of the work is outlined in the following diagram, in which d.c. represents determination of the physical constants and c.h. complete hydrogenation.



The complete hydrogenation of the aromatic compounds, especially the compounds with high molecular weight, is very difficult. As an upper limit for the temperature 310° C. was chosen. It has been proved that at this temperature there is practically no destruction.

The method of hydrogenation is the same for all fractions. The oil is brought into the autoclave in an atmosphere of carbon dioxide and

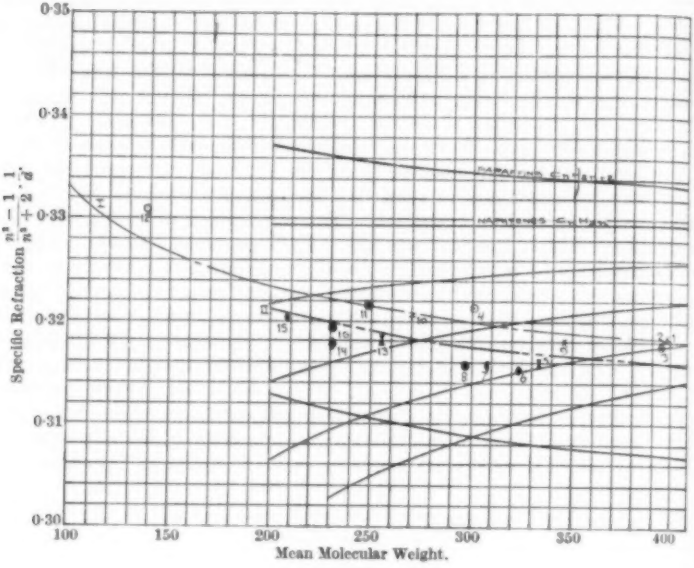


FIG. 1.

No.	Material (after complete hydrogenation).	Aniline point.	Average number of rings per molecule.	No.	Material (after complete hydrogenation).	Aniline point.	Average number of rings per molecule.
1	GR 70	97·2	3·8	9	GR 30	87·8	3·6
2	AR 70	95·8	3·9	10	AR 30	79·4	2·6
3	BR 70	95·1	4·0	11	BR 30	76·4	2·3
4	CR 70	88·7	2·6	12	CR 30	58·4	0·9
5	GE 70	82·8	3·9	13	GE 30	71·8	2·9
6	AE 70	78·5	3·9	14	AE 30	67·0	2·7
7	BE 70	76·5	3·7	15	BE 30	62·1	2·2
8	CE 70	76·7	3·6	16	CE 30	66·3	2·5

about 10 per cent. of the nickel catalyst added. After filling the autoclave with hydrogen at a pressure of about 100 kg./cm.^{2}, the temperature is increased to 310° C. and maintained at this value until the pressure, reduced to 0° C., does not further decrease. In most cases the product of reaction in the autoclave is dissolved in benzene. Pentane was used for the low molecular fractions to prevent losses of the volatile compounds

of the product. The catalyst was removed from the solution by filtration. As far as the volatility of the product permitted the benzene was removed under vacuum at 150° C., the pentane at a maximum temperature of 80° C. To ensure the absence of volatile reaction products in the benzene (pentane) after distillation, the n_D^{20} of the distillate was determined.

The complete hydrogenation of the oil, in most cases, was controlled by measuring the specific dispersion $\frac{n_{G'} - n_C}{d} \times 10^4$. For a saturated oil this constant has to be smaller than 158. As the extract contains more aromatic compounds and more sulphur than the refined products, the number of hydrogenations necessary for complete saturation of the oil is larger for the extract than for the refined product. The ratio is 20 to 5.

Survey of the Results.

Extract.—A survey of the properties of the raw material and of the reaction products obtained from this raw material (total reaction products) is given in Table I.

Table I.

	Raw material (extract).	AE Berginization.	BE Catalyst molybdenum.	CE Catalyst nickel.
n_D^{20}	1·59	1·593	1·5708	1·5680
d_4^{20}	1·0399	1·0293	0·9985	0·9968
$\frac{n^2-1}{n^2+2}\frac{1}{d}$ (D)	—	0·329	0·3290	0·3282
Mean molecular weight	317 (C_6H_8)	265 ($C_{19}H_8$)	234 ($C_{19}H_8$)	240 ($C_{19}H_8$)
S, %	0·48	—	—	—
Aniline point	About −15° C.	—	−8° C.	—
Bromine value (McIlhiney)	0	6	3	—

Table II.

Extract Experiments.

30% fraction of:	n_D^t.	t° C.	d_4^t.	$\frac{n^2-1}{n^2+2}\frac{1}{d}$ (D)	Mean molecular weight.*	Aniline point. Observed.	Aniline point. Read from graph.	Average no. of rings per molecule.
Raw material (extract).	1·5921	20·0	1·0269	0·3296	273	−15	—	—
Raw material after complete hydrogenation	1·4896	20·0	0·9082	0·3181	255	71·8	76·5	2·9
Berginization	1·5652	20·0	0·9857	0·3306	231	−9·5	—	2·7
Experiment with molybdenum catalyst	1·5370	20·0	0·9466	0·3299	195	−4·0	—	—
Ditto after complete hydrogenation	1·4770	20·0	0·8819	0·3204	209	62·1	—	2·2
Experiment with nickel catalyst	1·5412	20·0	0·9564	0·3287	204	−4·5	—	—
Ditto after complete hydrogenation	1·4836	20·0	0·8954	0·3193	231	66·3	—	2·5

* Mean molecular weight determined cryoscopically in benzene.

The physical constants of the six fractions obtained by distillation from the raw material and the reaction products have not been mentioned in this paper. However, it may be remarked that they demonstrate a regular change in properties for the successive fractions.

The further part of the investigation was carried out with the "30 per cent. fractions" (combination of the first two fractions) and the "70 per cent. fractions" (the combination of the fractions III, IV, V and VI). The physical constants of these products and their hydrogenation products are given in Tables II and III and Fig. 1.

TABLE III.

Extract Experiments.

70% fraction of:	n^t.	t° C.	d_4^{20}.	$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$ *	Mean molecular weight.	Aniline point. Observed.	Aniline point. Read from graph.	$\frac{n_C-n_F}{d}\times 10^5$.	Average no. of rings per molecule.
Raw material (extract)	n_D : 1·6024	20·0	1·0434	0·3289	325†	—	—	—	—
Ditto completely hydrogenated	n_D : 1·5037	20·0	0·9363	0·3161	334†	82·8	84·1	155	3·9
Berginization	n_D : 1·610	20·0	1·0529	0·3292	312	—	—	—	—
Ditto after complete hydrogenation	n_C : 1·50250 n_D : 1·50527 n_F : 1·51167 $n_{G'}$: 1·51716	20·1 20·1 20·1 20·1	0·9404	0·3155	324	78·5	81·8	156	3·9
Experiment with molybdenum catalyst	n_D : 1·5868	20·0	1·0307	0·3260	292	—	—	—	—
Ditto after complete hydrogenation	n_C : 1·50041 n_D : 1·50318 n_F : 1·50956 $n_{G'}$: 1·51499	20·15 20·15 20·1 20·1	0·9365	0·3158	309	76·5	80·4	156	3·7
Experiment with nickel catalyst	n_D : 1·5865	20·0	1·0315	0·3256	295†	—	—	—	—
Ditto after complete hydrogenation	n_C : 1·50199 n_D : 1·50484 n_F : 1·51134 $n_{G'}$: 1·51687	20·0 20·05 20·0 20·0	0·9385	0·3158	298†	76·7	78·8	158	3·6

* The specific refraction is calculated with the n_D^{20} observed with the Abbe refractometer. For the hydrogenated products in Table III the n determined with the Pulfrich refractometer is noted. In some cases there is a small difference between the value observed with the Abbe and with the Pulfrich refractometer.

† Determined in naphthalene; for the other values benzene was used.

Refined Product.—In the case of the refined product the method of investigation is quite analogous. The physical constants of the total reaction products are given in Table IV.

Also in this case the constants of the six fractions obtained by the distillations are not mentioned in this paper, but the successive fractions indicate a regular change in properties.

The further investigation was carried out with the 30 per cent. and 70 per cent. fractions. Tables V and VI represent the physical constants of these fractions and their hydrogenation products (see also Fig. 1).

TABLE IV.

	Raw material (refined product).	AR Berginization.	BR Catalyst molybdenum.	CR Catalyst nickel.*
n_D^{20}	1·5077 (50°)	1·5132	1·5060	1·4785
d_4^{20}	0·9290 (50/4)	0·9325	0·9249	0·8630
$\frac{n^2-1}{n^2+2}\frac{1}{d}$ . . .	0·3207 (50°) 0·3199 (20°, calc.)	0·3224	0·3212	0·3283
Mean molecular weight † .	398	315	327	213
S, %	0·11	—	—	—
Aniline point, ° C. . .	75·2	68·6	72·2	65·6
Bromine value (McIlhiney)	—	—	—	1·1

* The constants determined for this product cannot be compared with the analogous constants of the 30 per cent. and 70 per cent. fractions derived from it (see below). There was observed some alteration in the product.
† Determined cryoscopically in benzene.

TABLE V.

Refined Product Experiments.

30% fraction of :	n^t.	t° C.	d_4^{20}.	$\frac{n^2-1}{n^2+2}\frac{1}{d}$	Mean molecular weight.†	Aniline point. Observed.	Aniline point. Read from graph.	$\frac{n_D - n_C}{d} \times 10^4$.	Average no. of rings per molecule.
Raw material (refined product)	n_D : 1·5183	20·0	0·9495	0·3193	356	66·9	—	—	—
Ditto after complete hydrogenation	n_C : 1·49039 n_D : 1·49308 n_F : 1·49923 $n_{G'}$: 1·50449	20·0 19·95 19·95 20·0	0·9139	0·3180	346	87·8	89·1	155	3·6
Berginization experiments	n_D : 1·5004	20·0	0·9026	0·3261	247	54·1	—	—	—
Ditto after complete hydrogenation	n_C : 1·47778 n_D : 1·48044 n_F : 1·48640 $n_{G'}$: 1·49148	20·1 20·1 20·1 20·1	0·8872	0·3205	270	79·4	83	155	2·6
Experiments with molybdenum catalyst	n_D : 1·4912	20·0	0·8917	0·3249	232	55·4	—	—	—
Ditto after complete hydrogenation	n_C : 1·47308 n_D : 1·47564 n_F : 1·48151 $n_{G'}$: 1·48653	20·15 20·15 20·15 20·15	0·8769	0·3215	249	76·4	81·3	153	2·3
Experiments with nickel catalyst	n_D : 1·4408	20·0	0·7946	0·3322	134	45·0	—	—	—
Ditto after complete hydrogenation	n_D : 1·4339	20·0	0·7872	0·3308	139	58·4	—	—	0·9

* See note * to Table III.

† Determined cryoscopically in benzene.

TABLE VI.

Refined Product Experiments.

70% fraction of:	n^t.	$t°$ C.	d_4^t.	$\frac{1}{n_a^2}\left\|\frac{n_a}{d}\right\| + \frac{n_a}{n_a^2}$	Mean molecular weight.†	Aniline point. Observed.	Aniline point. Read from graph.	$\frac{n_{G'} - n_C}{d} \times 10^4$.	Average no. of rings per molecule.
Raw material (refined product)	n_D : 1·5192	20·0	0·9482	0·3202	405	77·3	—	—	—
Ditto after complete hydrogenation	n_C : 1·49034 n_D : 1·49319 n_D : 1·4969 (Abbe) n_F : 1·49918 $n_{G'}$: 1·50415	30·3 30·3 20·0 30·3 30·3	0·9183	0·3196	398	97·2	96·4	152	3·8
Berginization experiments	n_D : 1·5189	30·0	0·9458	0·3209 (30°) 0·3206 (20°)	395	75·4	—	—	—
Ditto after complete hydrogenation	n_C : 1·49258 n_D : 1·49521 n_D : 1·4990 (Abbe) n_F : 1·50128 $n_{G'}$: 1·50635	30·3 30·3 20·0 30·3 30·3	0·9232	0·3180	396	95·8	95·0	151	3·9
Experiment with molybdenum catalyst	n_D : 1·5144	20·0	0·9432	0·3194	394	78·8	—	—	—
Ditto after complete hydrogenation	n_C : 1·49314 n_D : 1·49588 n_D : 1·4994 (Abbe) n_F : 1·50204 $n_{G'}$: 1·50708	30·3 30·3 20·0 30·25 30·3	0·9252	0·3176	395	95·1	94·0	152	4·0
Experiment with nickel catalyst	n_D : 1·4941	20·0	0·9019	0·3228	297	76·7	—	—	—
Ditto after complete hydrogenation	n_C : 1·47952 n_D : 1·48215 n_F : 1·48807 $n_{G'}$: 1·49302	20·4 20·4 20·4 20·4	0·8883	0·3214	301	88·7	89·1	152	2·6

* See note * to Table III.

† Determined cryoscopically in benzene.

CONCLUSIONS.

From the survey of the total reaction products (Tables I and IV) it can be concluded that the destructive hydrogenation of the refined product always caused a decrease in the mean molecular weight. In the experiment without a catalyst and using molybdenum as a catalyst, the mean intensity of destruction was about equal. However, in the case of the experiment with nickel as a catalyst the mean molecular weight was much lower. Also in the case of the extract there was always some destruction, the smallest being for the experiment without a catalyst. Here, nickel and molybdenum had about an equal effect. Therefore, in this case the activity of the nickel is not pronounced as in the case of the refined product. (However, it may be remarked that in the experiment with the refined product a small trace of a destruction catalyst from a previous investigation may have contaminated the walls of the autoclave.)

The 70 per cent. fractions obtained from the refined product experiments

(except for the nickel experiment) demonstrate that the mean molecular weight of the higher molecular fractions was equal to the mean molecular weight of the 70 per cent. fraction of the raw material. Also, the other properties indicate a good resemblance. The differences must, therefore, be found in the 30 per cent. fractions. Indeed, the 30 per cent. fractions of the reaction products have a much lower mean molecular weight than the 30 per cent. fraction of the raw material. In the case of the experiment with nickel as a catalyst there is a destruction over the whole range.

Also in the case of the extract there is a more regular destruction over the whole range; both the 30 per cent. and the 70 per cent. fractions of the reaction products have a lower molecular weight than the corresponding fractions of the raw material.

It may be remarked also that the products of the experiments in which a catalyst (nickel or molybdenum) was used appeared to be more saturated than the products of the berginization experiment (relatively low n_D^{20}, d_4^{20} and specific refraction, high aniline point).

The physical constants of the six fractions that were obtained by distillation of the raw materials, and their reaction products demonstrated a regular change with increasing molecular weight. Therefrom it may be concluded also that the composition of the fractions does not show a sudden or irregular change. This fact makes the results for the 30 per cent. and 70 per cent. fractions more important.

The experiments have proved that under the given conditions *there is practically no change in the total amount of rings* of the product. Only in the case of the nickel experiment of the refined product is a small loss in the amount of rings observed. However, the average number of rings per molecule decreases with decreasing molecular weight. If only the *total amount* of rings is considered and *not the unsaturation* of the rings (and paraffinic chains), the specific refraction–molecular weight diagram can be used for the 30 per cent. and 70 per cent. fractions after complete hydrogenation. The specific refraction and the molecular weight of the 30 per cent. and 70 per cent. fractions of the refined product in this diagram (see Fig. 1) approximately form points of one curve. For the extract also an analogous curve can be constructed. Only the points of the nickel experiment of the refined product (4 and 12 in Fig. 1) indicate a deviation. However, it has already been stated that in this case there was some loss of rings. The curves for the raffinate fractions and the extract fractions are nearly parallel.

An analogous relation between specific refraction and molecular weight has been described in a previous communication.[5] In this case, however, the result was obtained in a quite opposite way—namely, by polymerization of *cyclo*hexene.

Both for the refined product and the extract the final results of the destructive hydrogenation under the given conditions may be explained by a regular destruction of the molecules, in which the molecules have been split in analogous parts. This destruction may be considered as a "depolymerizing" action.

In Fig. 1 the curve I indicates the change of the specific refraction with decreasing molecular weight for such a regular destruction of a mixture of hydrocarbons with the composition of the refined product (the

specific refraction determined after hydrogenation). In the same way, curve II indicates these values for the destruction of the extract. These curves support the previous conclusions.

However, a petroleum chemist will compare the cyclic character of the original lubricating oils (the *total* extract and refined product) with the lubricating oils obtained from the reaction products (the 70 per cent. fractions). This comparison can similarly be made from Fig. 1, and in this case also the differences in cyclic character are small.

We acknowledge our thanks to Dr. A. J. Tulleners, Ir. P. C. Kruyff and Ir. W. J. K. Schönlau, for the execution of the first part of this investigation.

Delft, Laboratory of Chemical Engineering of the University.
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